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BLEACHING AND FINISHING
OF COTTON.

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THE PRINCIPLES OF BLEACHING AND FINISHING OF COTTON.

BY

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AND

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With 240 Illustrations.

THIRD EDITION, REVISED, ENLARGED, RE-SET

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PREFACE TO THIRD EDITION.

THE exhaustion of the second edition may be regarded as an indication that this book has established a position in the literature of cotton bleaching. The present edition has been rewritten and brought up to date, but the large amount of work which has been published during recent years has made the selection of matter for inclusion difficult Special mention must be made of the valuable publications of the Cotton Research Association, and of the courtesy of the Association in supplying information and illustrations. It is hoped that adequate acknowledgment has been made in the text of its work and that of all other authors.

S. R. T.

NOTTINGHAM,
September 1927

PREFACE.

BLEACHING and finishing, like many other trades resting on a chemical basis, were founded on empiricism, and are still largely controlled by it It is perhaps remarkable that the practice taught by generations of empiricism has, in general, proved to be based on sound scientific principles. The success obtained by the devotees of the rule of-thumb *cum* experience school of workers has in bleaching, as in many other chemical industries, tended to the belittling of the value of scientific knowledge. The chemist, on the other hand, has been sometimes apt to underrate the value of inherited experience and to think that all the difficulties which arise in practice can be successfully solved purely by the application of a knowledge of the chemistry of the processes involved. In bleaching, and still more in finishing, practical experience can hardly be

under-estimated; but neither can it be gainsaid that empiricism has nothing to lose and everything to gain from a working alliance with science. The fundamental reason why the theoretical and the practical treatment of the subjects here considered are so frequently regarded as being incompatible is, that the devotee of either system is confronted with difficulties arising out of ignorance of the resources and methods of the system which is complementary to his own.

The following pages deal with the principles underlying the practice of bleaching and finishing and the chemistry of the processes involved. A knowledge of the latter is essential to the successful carrying out of original constructive experiments, without which it will be very difficult in the future to make much advance in practice.

We have endeavoured to present the two aspects of the subject in their complementary relations, with the particular object of assisting the practical student to appreciate the functions of the processes he is called upon to control, in their relation to the results ultimately aimed at.

The scope of the subjects brought into relation necessitates some curtailment in the treatment adopted with regard both to laboratory and workshop routine, as the object is to correlate principles rather than edit recipes. The latter are often of but temporary and isolated value, whereas the scientific adaptation of cause to effect by the aid of real acquaintance with the controlling factors is always, whether consciously or otherwise, the basis of successful working.

The examples of methods given are introduced as practical illustrations of the sequence of the various processes described. Although they are taken from actual practice, they are in some cases at variance with the principles laid down in these pages It is in just such cases as these that a knowledge of the chemical and physical principles underlying the processes can usefully find employment.

S R. T.
E. L. T.

NOTTINGHAM,
April 1911.

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BLEACHING AND FINISHING OF COTTON.

CHAPTER I

INTRODUCTION.

COTTON consists essentially of cellulose As received by the bleacher, it contains, also, all the natural constituents of the cotton fibre, together with adventitious impurities introduced during the processes of manufacture Bleaching may be defined as the removing of all these natural and adventitious impurities and leaving a residue of pure cotton in which all its valuable properties, as a textile fibre, are fully developed and in which no destruction or alteration of the cotton cellulose has taken place Natural twist, tensile strength, and elasticity must be unimpaired; lustre and permeability must be highly developed; the natural white colour of pure cellulose must be produced. All this must be done without altering the physical or chemical properties of the cellulose. The success of the operations may be measured by the purity and durability of the white colour of the final product, and by the extent to which the properties mentioned above have been maintained or developed. Goods are, however, sometimes only partially purified and bleached, the residual colour being disguised by the use of a blue substance such as smalt, ultramarine, or a suitable dye The natural constituents of cotton, other than cellulose, are protoplasmic and other nitrogenous compounds, oil, wax, pectins, tannin, colouring matter, and mineral salts During manufacture, such things as dirt, mineral and other oil, sizing such as starch, glue, Irish moss, or antiseptics, are also introduced. Some of these impurities are soluble in water but most of them are not. The soluble impurities may be removed by washing The remainder must be converted by chemical processes into bodies soluble in, and capable of being removed by washing with, water After this has been accomplished the goods are finally washed, with or without soap, and finished as required. Finishing may consist entirely of mechanical processes the object of which is to develop or modify the physical properties of the cotton cellulose, or it may involve, also, the addition to the cotton of such substances as starch, dextrin, mineral matters, fireproofing or waterproofing mixtures, or antiseptics.

Although the chemistry of bleaching is fairly simple it is none the less important, and the successful bleacher is he who understands fully the chemical principles involved and can supplement his knowledge with actual practical experience. Experience alone, without chemical knowledge, can be of comparatively little use in dealing with a problem which presents any unexpected or obscure difficulties, but which can be often overcome readily by the application

of scientific knowledge. Methods founded upon experience alone may give good results as long as the conditions remain constant.

Changing, and more especially unknown, conditions can only be met successfully by chemical investigation combined with experience. Two things are essential to the mental equipment of the bleacher. The first is some knowledge of the chemistry and physics of cotton itself, and of the various processes and materials used in its treatment; the second is the ability to carry out constructive experiments based upon the knowledge gained by the study of the chemistry of the processes themselves and the materials used. A knowledge of the chemistry of the processes will prevent many faults being committed, and the information gained by analysis of the materials employed will assist further in the production of good results, but both require to be supplemented by practical constructive experiments carried out either in the laboratory or the bleach works if the trade is to be carried on upon a scientific basis. It must be added that much patience and many disappointments are to be expected and endured in the pursuit of science. Chemistry is no magician's wand that will cause difficulties to vanish immediately. The practical bleacher who is confronted by a problem which he cannot solve by the light of experience alone must not expect the application of even a fairly extensive knowledge of chemistry to give him instant relief from his difficulty, nor become discouraged or impatient if it even fails to do so His attempt to solve a difficult problem upon the right lines will, even if at the time unsuccessful, equip him better to tackle it again or to solve the next that presents itself.

CHAPTER II.

THE NATURE, GENERAL PROPERTIES, AND CLASSIFICATION OF TEXTILE FIBRES.

THE number of fibres used for textile purposes is very large. They have all one property in common, namely, that of being capable of being spun into yarn and woven or knitted into fabrics They are both natural and artificial, and may be classified roughly according to their origin as—

1 Vegetable fibres, such as cotton, flax, jute, hemp, ramie
2 Animal fibres, such as silk, wool, hair
3 Artificial fibres, such as viscose silk.
4 Mineral fibres; such as asbestos

Naturally occurring fibres must be found, or grown easily, in large quantities, while artificial fibres must be manufactured cheaply enough to compete with those of natural origin Fibres which cannot be produced cheaply, or in large quantities, can have only a very limited value for textile purposes. Spider's-web would be a perfect textile fibre, but the quantity available is too small to make it worth the cost of manufacture.

The value of a fibre for textile purposes is determined, largely, by the degree to which it possesses certain fundamental properties, viz tensile strength, elasticity, and spinning power. Tensile strength and elasticity are essential to enable the fibre to withstand the strain of spinning into yarn, weaving or knitting into fabrics, and to give the finished fabric sufficient strength for the purposes for which it is designed Less tensile strength is required in the individual fibres of a fabric than in the raw fibres or in a yarn, because they give each other mutual support Fibres which are deficient in strength are sometimes strengthened during the manufacturing processes by "sizing" with a solution of a colloidal substance such as starch, glue, or gum which can be washed out of the finished fabric Woven fabrics contain two kinds of threads, warp and weft. The warp threads run throughout the length of the fabric, forming the skeleton and taking the strain of manufacture or wear These must possess a high degree of tensile strength and elasticity. The weft threads run transversly, filling up the spaces between the warp threads. They give body to the fabric but do not take the strain of wearing to the same extent as the warps. Fibres or yarns which have insufficient strength for warp may be used for weft, especially if sized before weaving. Further information may be found in Bowman's *Structure of the Cotton Fibre.*

Spinning power depends primarily upon tensile strength and elasticity, but also upon other properties such as (1) length of fibre, (2) fineness or diameter, (3) evenness of length and diameter, (4) presence of natural twist or roughness to help the fibres to hold together. Spinning may be defined as the laying of

the fibres parallel to one another and twisting them together round a longitudinal axis There are exceptions, as in the of case woollen yarns, but the definition applies to all cotton yarns

It is difficult to twist short fibres together and, when twisted or spun, they do not resist tension like long ones. Fibres which are too short to spin alone, may be spun if mixed with longer ones, but high-grade yarns are always prepared from fibres of approximately the same length These are obtained from the raw fibres by processes termed " carding " and " combing "

Fineness and regularity of diameter are also important. Yarns are spun to give a fixed relation between weight and length, termed " count " This implies an approximately constant thickness or diameter. The value of a yarn is determined largely by the regularity of its diameter. But this, in turn, depends upon the regularity of the diameter of the individual fibres. The cross-section of a yarn must contain enough fibres to give it the required strength This number does not vary much in fine and coarse yarns It follows, that fine yarns can only be made from fibres of small diameter. Thus from one pound of a low-grade cotton we may not be able to spin more than 33,600 yards of yarn, while from the same quantity of a high-grade Sea Island cotton ten times this length may be obtained The length of commercial textile fibres varies from one half to four or five inches Their diameter is rarely more than $\frac{1}{1000}$ of an inch.

Natural twist, or roughness, helps the fibres to hold together. Perfectly smooth and frictionless fibres would be difficult to spin, and the yarn would offer but little resistance to longitudinal tension The individual fibres would be easily drawn out All textile fibres have a natural twist, curl, or roughened surface Thus cotton has a highly developed twist, flax a rough and jointed surface, and wool has scales with free projecting edges and also a natural curl.

In addition to these basic properties, there are others which are important, and determine, also, the value of a fibre and the purpose for which it may be used These include (1) softness, (2) suppleness or flexibility, (3) lustre, (4) permeability to solutions of dyes, etc , (5) absence of colour or degree of resistance of natural colour to bleaching, (6) resistance to decay The properties of a textile fibre designed for sack cloth or string are obviously of a different order to those of a fibre intended for a lace or a dress material In the first case strength, elasticity, and durability are the chief requirements. Colour, softness, permeability are unimportant. On the other hand, a fibre for a dress material must be soft, supple, lustrous, permeable, and devoid of natural colour or easily bleached.

Some natural fibres possess more of these properties than others Silk has all, wool and cotton have many, ramie has several, but is so deficient in others, such as softness, that it cannot be worn next the skin

These properties may be latent in the natural fibre but can be developed during the preparatory processes, or after manufacture of the yarn or fabric. Thus, softness, lustre, and permeability only become apparent when the naturally occurring or adventitious impurities are removed by physical or chemical processes.

Coloured fibres may be rendered white by scouring and bleaching. Sometimes a property in which a fibre is deficient may even be imparted to it by a suitable physical or chemical process Thus, the lustre of cotton can be increased by the processes of schreinerising or mercerising. Each textile fibre demands different treatment to bring out all its properties. The object of this treatment

is always the same—that is, to leave the fibre with its properties highly developed without, at the same time, damaging its value for textile purposes. For purposes of study textile fibres may be grouped as follows :—

1. Unicellular cellulose fibres—cotton
2. Multicellular cellulose fibres—flax, ramie, hemp, jute, posidonia, etc
3. Animal secretions—silk
4. Appendages of the epidermis of animals—wool, hair, fur.
5. Artificial fibres -lustracellulose, viscose, cellulose-acetate
6. Mineral fibres—asbestos

Cotton is the only unicellular fibre of much commercial importance Each fibre is a single complete vegetable cell forming a hair on the cotton seed. It is produced for the special purpose of assisting in the distribution of the ripe seed Its structures and properties will be dealt with fully later. Other members of this class are kapok, mudar or yercum, silk cotton or semal cotton. They are all plumose fibres (*i e* hairs) from the seeds of plants. Kapok hairs are produced by the seeds of the kapok tree, which grows in India, Ceylon, South America, and Africa It is a silk-like hair, which is, however, too short for spinning, its length being only about half an inch. It is used for other purposes, such as stuffing mattresses Mudar or yercum fibres come from an Indian plant They are short and silky, and have little spinning power Semal cotton consists of the seed hairs from Indian *Bombax malabaricum*.

Multicellular Vegetable Fibres.—These fibres, unlike cotton, consist of many cells joined together Moreover, they are not, like cotton, hairs attached to the seed of a plant, but part of the stem or other tissue. They are not, therefore immediately available for spinning, but must be separated, first, from the stem or tissue of which they form an integral part The multicellular fibres all consist of the ultimate "bast fibres" obtained from the inner lining of the fibrous bark of a plant Flax may be taken as an example The flax plant belongs to the natural order Linaceæ, and species *Linum usitatissimum* It is widely distributed, and is cultivated commercially in many countries, including Belgium, Holland, England, and Ireland Courtrai flax, the most valuable variety, is grown in Belgium

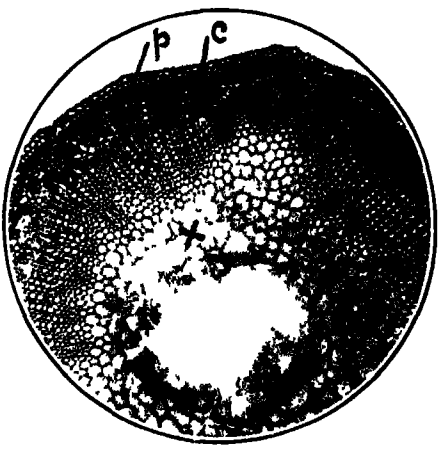


FIG 1.—Transverse section of flax

The plants, which are herbaceous, are grown each year from seed. When ripe they are pulled out of the ground and allowed to wither The stalks, leaves, and seed are then separated from one another by combing The seed when pressed yields linseed oil, the residue being made into cattle cake The withered stalks contain about 75 per cent. of bast fibres. A transverse section of a flax stalk is shown in fig 1.

The outer layer consists of cuticle; beneath this is the cortex, *c*. In the

centre is the harder lignified tissue known as the xylem, *x*, and between this and the cuticle comes the softer tissue, or phloem, *p*, which is actively growing, and through which the cell sap, containing the dissolved food matter, is conveyed. Immediately above the xylem is a layer of cells termed the cambium, *cb*, and in the tissue above this are bundles or groups of cells, which constitute the bast fibres, *b*. The first process in the separation of the bast fibres is termed "retting." The object of this is to break down the structure of the stem and dissolve the cementing substances which hold the various tissues together. There are three kinds of retting processes, viz. (1) water retting, (2) dew retting, (3) chemical retting.

In water retting, the stalks are tied in bundles and covered with water in a tank. Putrefactive fermentation, caused by bacteria, soon sets in This softens the stalks, owing to the decomposition of the outer less-resisting tissues and solution of the intercellular cement. When the fermentation has proceeded far enough, the bast fibres can be separated from the rest of the stalk. If the fermentation be carried too far the bast fibres may be damaged. This is prevented by careful inspection and control of the process, which takes about three weeks for completion.

Dew retting is similar in its action, but slower. The stalks are spread on grass to ferment and, if necessary, moisture is supplied by occasional watering. Sometimes fermentation is started by water retting and completed by dew retting.

Chemical retting consists of boiling the stalks with acid or alkali, with or without pressure, and then washing away with water the soluble bodies produced by the chemical action The process is quicker than either of the other two. After retting, the stalks, or retted flax, are passed between rollers, to squeeze out the excess of water and soluble impurities, and are then washed and dried

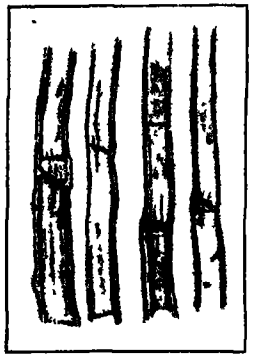


Fig 2.—Flax fibre.

Breaking is the next operation The dried stalks are crushed by means of pairs of horizontal fluted rollers which break up the woody tissue, or xylem, into small fragments, leaving the less brittle bast fibres undamaged After "breaking," the crude fibres are separated from the broken woody fragments by a process termed 'scutching." This may be done by simply beating the broken stalks by hand till the woody tissue is removed, or by a machine specially designed to produce a similar beating effect

The scutched flax is then "hackled." This is a combing process which finally separates the bast fibres and lays them parallel to one another, removing, at the same time, the short fibres The hackled flax is drawn out and spun in a similar manner to cotton.

The fibres vary in length from 1 to 3 inches. Each fibre is composed of a large number of fibrils consisting of cells joined together. These have an average length of about 1 inch, and a diameter varying from $\frac{1}{1000}$ to $\frac{1}{3000}$ of an inch.

Microscopic Structure.—The ultimate flax fibre has the appearance of a straight tube with thick cell walls and a narrow but distinct lumen (fig. 2). The end of the fibre appears to be pointed, while on the outer surface longitudinal striations are visible. The cross-section is polygonal in shape. Nodes

or swellings are visible on the surface of the fibre, giving it a jointed appearance. Where these joints occur, as well as at other points, transverse divisions will often be seen across the fibre, placed somewhat obliquely to its longitudinal axis. Both the joints and transverse partitions are rendered more visible by mounting the fibre in iodine-sulphuric acid or zinc-chlor-iodide solution. No natural twist can be seen, but the apparently rough surface of the fibre and its jointed structure assist in spinning.

Ramie consists of bast fibres from the ramie plant, or China grass, a species of *stingless* nettle which is cultivated in China, Japan, India, South America, and other places. The plant, or shrub, grows to a height of from 4 to 8 feet. It is hardy, grows rapidly, and yields three or four crops each year. The preparation and properties of the fibre have been described fully by Marshall (*J. Soc Dyers and Col.*, 1922, p. 293), from whose paper the following details are taken.—

After the plants are cut down they are "decorticated." This consists of removing the outer bark and separating the bast fibres in the form of ribbons,



FIG. 3.—Ramie fibres.

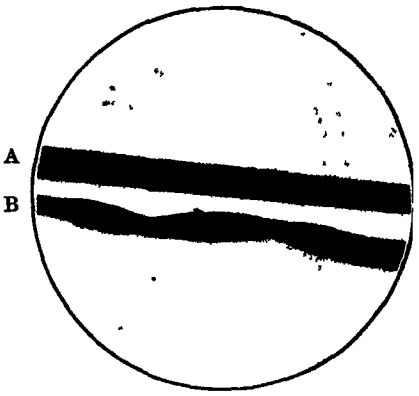


FIG. 4.—Mercerised ramie fibres.

A, Single ramie fibre mercerised under full tension.
B, " " " without tension.

which are hung out to dry. This process is carried out largely by hand, the stems being first soaked in water, and the bark scraped off with a knife, a ring, or the fingers. The dried decorticated material forms commercial China grass. The decorticated fibre is "degummed" to remove the impurities. The process is very similar to that used for scouring cotton, which will be described later.

Microscopic Structure.—Ramie fibres are similar to flax but coarser and more irregular, with a wide, well-marked lumen (fig. 3). Bleached ramie is white, soft, and highly lustrous. It has a higher tensile strength than any other vegetable fibre, and is also more durable, but it has not the flexibility of cotton. The individual fibres lack the power of cohesion. This causes yarns spun from ramie to be hairy, diminishes their lustre, and makes them unsuitable for wearing next the skin. Moreover, owing to lack of flexibility, ramie has a tendency to

break. The following table shows the chief physical properties of ramie compared with other fibres:—

	Ramie	Flax.	Cotton.	Hemp.	Silk
Tensile strength .	100	25	12	36	13
Elasticity	100	66	100	75	400
Torsion	100	80	400	95	600

According to Marshall (*loc. cit.*), mercerisation of ramie yarns, or piece goods, produces an increased lustre and a loss of hairiness. But it has also another interesting effect it produces a twist similar to that of cotton. This, however, is only the case when the mercerisation is carried out without tension. This effect is shown in fig 4.

Animal secretions, such as silk, are solidified viscous liquids produced by silkworms and other caterpillars, spiders, or certain shellfish. They differ from other fibres in two important respects they are continuous, or of indefinite as opposed to definite length. Thus, a silkworm may spin 3000 yards of silk without a break Since they are solidified, or coagulated, liquids they are not composed of cells and are comparatively devoid of structure, having generally a cylindrical homogeneous appearance when seen under the microscope.

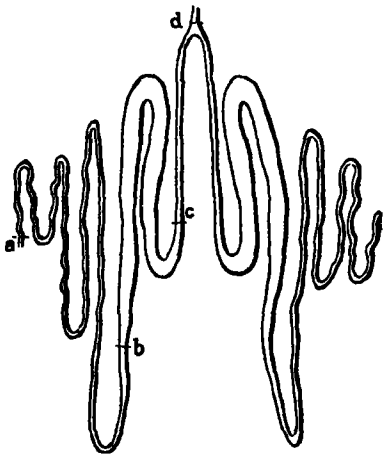


Fig. 5.—Silk glands

The silk fibre consists of an inner core of fibroin, or silk, and an outer sheath of sericin, or silk gum A considerable part of the body of the mature silkworm is occupied by the silk glands These are convoluted and cylindrical in shape and placed on each side of the body (fig 5). Each gland is provided with a duct, which leads to an orifice, termed the spinneret, in the lower lip of the larva The gland is filled with a viscous fluid, which coagulates on coming into contact with the air A separate thread, or brin, is produced by each gland. These are cemented together as they solidify, forming a double thread or bave. When this is examined under the microscope it is seen to consist of two cylindrical threads each of which has a somewhat opaque outer sheath (fig 6) In places the two threads may be separated temporarily. The outer sheath constitutes about one-quarter of the fibre and consists of sericin or silk gum Its definition becomes plainer if the silk be soaked in cold dilute hydrochloric acid before examination. The inner portion of the fibre is the true silk or fibroin. Although this appears to be structureless, it consists in reality of a large number of fibrils cemented together.

These become visible only when the silk is treated with a chemical reagent such as an alkali, when they form small knots known as flocons or pelotons (fig. 7).

Tussur, a wild silk, differs from true silk in that the fibrillar structure can

be seen plainly without the aid of chemical reagents (fig. 8). It has, also, an irregular cross-section and a distinct twist like that of the cotton hair.

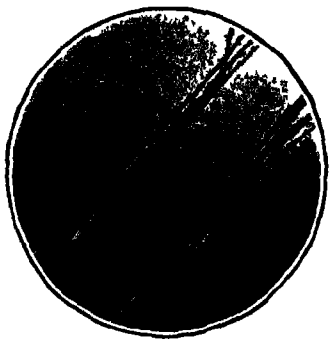


FIG 6.—Raw silk.



FIG. 7.—Flocons

Herzog (*Chem. Zeit*, 1923, vol. iv. p. 237) has stated, as a result of examining silk by means of X-rays, that it is built up of minute crystals, one axis of which runs parallel to that of the fibre. It was thought, at one time, that the silk glands contained a single fluid, which, as it exuded from the spinneret, became superficially oxidised to sericin, the relation between fibroin and sericin being supposed to be

$$C_{15}H_{23}N_5O_6+O+H_2O=C_{15}H_{25}N_5O_8.$$

Other observers held that the glands contained both fibroin and sericin in a liquid state. Thus, Georgevics states that if the silk gland be cut through at its thickest part, it will be found to consist of two distinct portions- an internal transparent layer, and an external portion which is colourless, greenish, or yellow according to the breed of the worm, and which occupies about one-quarter of the total volume. This outer layer is the sericin, and the inner the fibroin. But it is difficult to understand how one gland could produce two distinct liquids. Later researches appear to prove that the worm has two pairs of glands Those described above secrete the fibroin. Placed near the head of the worm are two others, with ducts which open at the spinning orifice. As the thread of fibroin issues from the silk glands it is covered with the secretion of the second pair, which when it solidifies forms the sheath of sericin and cements the two threads together.

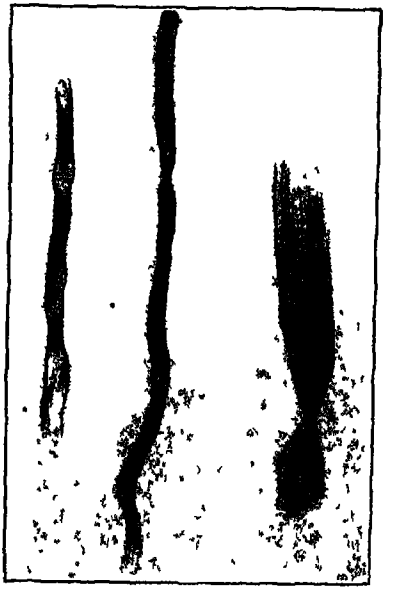


FIG. 8.—Tussur silk.

The way in which the liquid secretion coagulates is also somewhat uncertain. It cannot be mere drying, for there is no loss of water during the process. It was

thought by Dubois that the change is due to an enzyme, and is similar to that which takes place when blood clots. This is known to be due to the action of an enzyme termed thrombase. Foa (*J.S C.I.*, 1912, p. 224) gives another explanation, namely, that solidification is caused by mechanical strain during the ejection of the viscous secretion through the spinning orifice. He proved that it could not be due to mere exposure to air by drawing out several metres of silk from a worm entirely under water.

Both sericin and fibroin are allied closely to the proteins, being classified generally as scelero-proteins. But the sericin, or silk gum, resembles gelatin in many of its properties. Thus it swells up and ultimately dissolves in hot water, and more readily in the presence of soap or a mild alkali such as sodium carbonate It is removed from silk by these means.

Appendages of the epidermis of animals, such as wool and hair, are multicellular fibres consisting of the same kinds of cells as those of the epidermis,

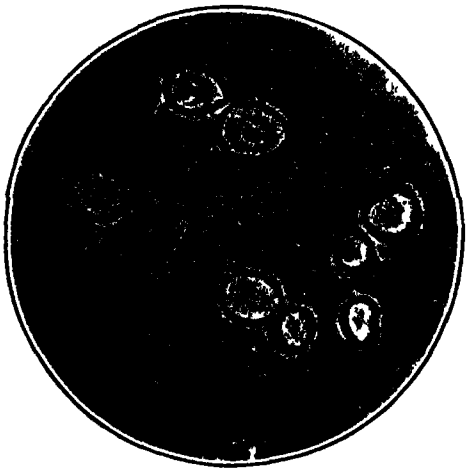


FIG. 9.—Wool fibre, transverse section

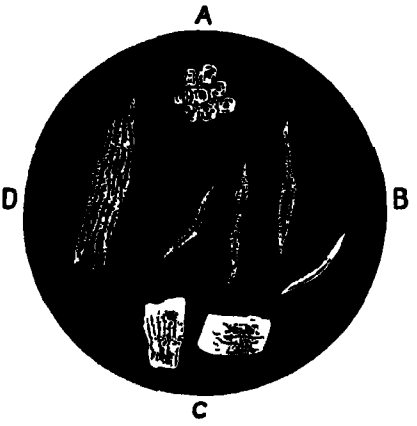


FIG 10.—Cortical cells.

A, Cells from medulla with nuclei and fat globules.
B, „ „ cortical substance with elongated nuclei and pigment cells.
C, Structureless horny scales from the cuticle (*After* Bowman)

from which they are produced. A transverse section of a wool fibre (fig. 9) shows three different types of cell In the centre are some rather large polygonal cells forming the medulla. External to this is the cortex, the cells of which are more compressed. Their cross section is polygonal also, but as they come nearer the periphery of the fibre they appear gradually flatter, becoming, ultimately, transformed into horny scales which form the outermost layer, termed the cuticle or epithelium.

When the cortical cells are teased out they are seen to be long and spindle-like, whilst those of the cuticle are flat, horny plates (fig. 10).

In wool, these epithelial scales have imbricated edges, pointing towards the tip of the fibre. Moreover, they are not completely adherent to the cortex, but have free serrated edges which overlap the adherent portions of the adjacent scales. These are illustrated in fig. 11, which shows a high-grade wool fibre. It will be noted that the cortex cannot be seen through the epithelial scales.

In high-grade wool the medulla is almost indistinguishable from the cortex, being only occasionally visible. Hair and fur have the same structure as wool, but differ in details. The epithelial scales are smaller, more numerous, and have rounded instead of imbricated edges. Moreover, they are often completely adherent to the cortex. The medulla is also commonly visible. A human hair is shown in fig. 12.

The artificial fibres, or silks, are all derived from solutions of purified cotton or wood pulp, by either evaporation or coagulation. They are therefore continuous like silk, and structureless. They will be described more fully in a later chapter, but they include nitrocellulose silk, cuprammonium silk, viscose silk, and acetyl silk (or cellulose acetate).

Mineral Fibres.—Certain varieties of asbestos have a fibrous structure and are capable of being made into fabrics, which are used on account of their fireproof

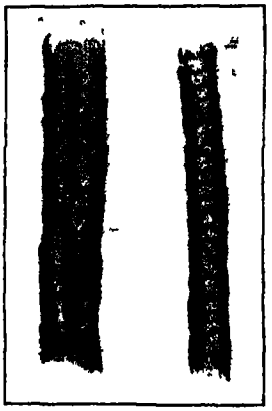


FIG 11.—Typical wool fibre.

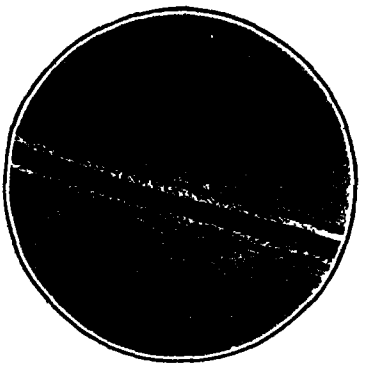


FIG 12.—Human hair

properties. But apart from these, mineral fibres are but little used for textile purposes

The different classes of fibres are readily distinguishable by means of the microscope. There are, also, certain chemical tests which may be employed.

Vegetable fibres, when purified, contain only traces of nitrogen, consisting almost entirely of cellulose. They burn readily with a luminous clear flame, unaccompanied by smell. When heated in a test-tube they are carbonised, and evolve vapours with an acid reaction. If treated with cold concentrated sulphuric acid they dissolve, and when the solution is warmed it becomes, at first, brown, then black, and finally swells up to a mass of carbon. Vegetable fibres do not dissolve in a boiling 5 per cent. solution of sodium hydroxide.

Animal fibres burn slowly and frizzle, giving off fumes with an unpleasant smell. When heated in a test-tube they swell up, forming a brownish-black sticky mass, and evolving fumes alkaline to litmus and smelling of ammonia. Heated with strong sulphuric acid, animal fibres dissolve but do not carbonise as readily as vegetable fibres. All animal fibres dissolve when boiled with 5 per cent. sodium-hydroxide solution. In the case of wool or hair the solution contains sodium sulphide, and gives a black precipitate of lead sulphide when treated with lead acetate solution. Silk which contains no sulphur does not give this reaction.

Artificial fibres if prepared from cellulose give the reactions of vegetable fibres, except that they generally burn more readily, those prepared from nitrocellulose being extremely inflammable. They may be distinguished from vegetable fibres by their greater lustre, and by the fact that when soaked in water they lose most of their tensile strength.

Mineral fibres, and sometimes heavily weighted natural fibres, will not burn. The latter, when ignited in a platinum or silica dish, leave an ash which generally retains the same form as the original material.

The group to which a fibre belongs may be determined by means of the following special tests –

Group 1—Cotton.—The characteristic constituent is cellulose. 1 When boiled with a 5 per cent. solution of sodium hydroxide cotton does not dissolve.

2 Cotton dissolves in cold concentrated sulphuric acid When the solution is warmed it blackens and swells up, forming a mass of black carbon. If the solution in cold sulphuric acid be poured into excess of cold water a precipitate (amyloid) is produced.

3. Cotton dissolves when warmed with a concentrated solution of zinc chloride. If this solution be diluted, a precipitate of cellulose is obtained.

4. Schweitzer's solution, especially if warmed, dissolves cotton readily. Schweitzer's solution is prepared as follows Dissolve 2 grammes of copper sulphate in 100 c c. water Add sodium-hydroxide solution till all the copper is precipitated. Then filter off the precipitated copper hydroxide and wash it with distilled water till it is free from alkali. Dissolve this residue in 20 per cent ammonia solution. The reagent does not keep well and should be freshly prepared as required. If the solution of cellulose in Schweitzer's reagent be poured into dilute acid, the cellulose is re-precipitated Tests 3 and 4 should be made with the material after boiling with sodium hydroxide Boiling sodium hydroxide removes impurities such as oil, which would delay or inhibit the action of the solvents.

5 Cotton gives a blue colour with iodine-sulphuric acid. This test is carried out as follows: Prepare the following solutions (1) Dissolve 1 gramme potassium iodide in 100 c c water and shake with iodine till a deep brown solution is obtained; (2) mix 20 c c. glycerine with 100 c c water and add 30 c c concentrated sulphuric acid To perform the test soak the fibre in the iodine solution. Squeeze out the excess of the reagent or remove it with blotting-paper, then immerse it in the sulphuric acid solution

6. Another useful reagent for detecting cellulose is zinc-chlor-iodine This is prepared by shaking iodine with a saturated solution of zinc chloride to which some potassium iodide has been added Cellulose is coloured blue when treated with this reagent

Group 2 contains two sub-groups. Hemp and jute are characterised by the presence of lignocellulose, while flax and ramie contain none All give the same general reactions as cotton, except that they dissolve much less readily in zinc chloride and Schweitzer's solutions. Lignocellulose is detected by soaking the fibre in a solution of aniline sulphate in water. If lignocellulose be present a yellow colour is produced. Jute is more deeply stained than hemp. When treated with iodine-sulphuric acid, fibres containing lignocellulose are coloured yellow.

Bleached cotton and flax may be distinguished by the following tests: (1) When soaked in a cold solution of potassium hydroxide, cotton is unchanged but flax generally becomes yellow. (2) Dry and soak in olive-oil Press out the excess of oil between blotting-paper. Flax will now be transparent and

cotton opaque. The reactions of ramie are the same as those of cotton. It is, however, easily distinguished by its appearance and feel.

Group 3—Silk.—1. Silk dissolves when boiled with 5 per cent. sodium-hydroxide solution. If lead acetate be added to the solution obtained no black colour or precipitate is produced.

2. When silk is warmed with strong hydrochloric acid (from 40 to 50 per cent.) it dissolves in about five minutes.

3. Silk dissolves readily in Loewe or Richardson reagent, slowly when cold or rapidly if warmed gently. These reagents are made as follows :—

Loewe Reagent.—Dissolve 10 grammes of copper sulphate in 100 c.c. water. Add 5 c c. glycerine and then 50 per cent. sodium-hydroxide solution till the precipitate of copper hydroxide first produced is just dissolved.

Richardson Reagent—Dissolve 25 grammes nickel sulphate in water. Add dilute (10 per cent) sodium-hydroxide solution till no further precipitate of nickel hydroxide is produced Filter off the precipitate and wash it with distilled water Then wash it into a 250-c c. flask with a little distilled water. Add 125 c c of strong ammonia solution (sp. gr. 0·88) and make up to 250 c.c. with water The solution must be shaken before use.

Both Loewe and Richardson reagents decompose on keeping and should be prepared frequently

Group 4- Wool.—1 *Wool is insoluble in concentrated hydrochloric acid* (40 to 50 per cent) even when warmed

2 Dilute alkalis, sodium and potassium hydroxides up to 5 per cent. strength, dissolve wool on boiling and slowly attack it when cold. Cold, strong (40 per cent.) sodium hydroxide, when allowed to act on wool for about five minutes, produces, after washing, an increased tensile strength and lustre. Strong alkalis when heated dissolve wool immediately. When lead acetate solution is added to the solution of wool in sodium hydroxide, a black precipitate of lead sulphide is thrown down.

3 If wool be boiled with a 10 per cent solution of copper sulphate, squeezed and treated with dilute sodium-hydroxide solution, a violet colour is produced. This is known as the biuret reaction, and is given also by silk.

4 Animal fibres, silk and wool, when boiled in a decolorised solution of magenta and washed in water are dyed pink. Vegetable fibres are not dyed by this reagent. Decolorised magenta is made by dissolving magenta in water and passing sulphur dioxide into the solution till the colour is just discharged.

Group 5.—Artificial silks give the general reactions for cotton. They are insoluble in boiling sodium hydroxide or in Loewe or Richardson reagents. They are all dissolved by concentrated cold sulphuric acid and are stained blue by iodine and sulphuric acid. Nitrocellulose silk, owing to the presence of nitro (NO_2) groups, gives a blue colour with a solution of diphenylamine in concentrated sulphuric acid Acetyl silk is soluble in acetone. When heated with sodium-hydroxide solution it is saponified, sodium acetate and cellulose being formed. If the mixture be filtered and concentrated, acetic acid may be identified by the following test. After careful neutralisation, a little neutral ferric chloride solution is added. In the presence of acetic acid a red colour due to ferric acetate is produced When the solution is boiled, the iron is completely precipitated as reddish-brown basic acetate and acetic acid is given off, which can be identified by its smell.

$$Fe_2(C_2H_3O_2)_6+2H_2O=Fe_2(C_2H_3O_2)_4(OH)_2+2C_2H_4O_2.$$

If an artificial silk be neither nitro silk nor cellulose acetate, it is either viscose

or cuprammonium silk. These may be distinguished as follows: Place about 0·2 gramme of the sample in a test-tube with 10 c.c. of concentrated sulphuric acid. Both kinds dissolve. In the case of viscose a reddish-brown colour is produced in from one to two minutes, and the silk dissolves, forming a brownish liquid. Cuprammonium silk gives a yellow colour, changing, through yellowish red, to a pale brown solution. This kind of silk often contains traces of copper, which serve also for its identification.

CHAPTER III

NATURAL HISTORY OF COTTON; VARIETIES AND CLASSIFICATION OF COMMERCIAL COTTON; BLENDING, BUYING, AND SPINNING.

COTTON is one of the oldest and most important of vegetable fibres. It has been grown and used in India and China for at least two thousand years. It was known, also, to the Egyptians, and was found in cultivation in the West Indies, Mexico, and South America by Christopher Columbus and other explorers. Its cultivation was introduced into North America by the early settlers.

Natural History of Cotton.

Cotton grows best between the parallels of latitude 45° N and 35° S. These include Asia, Africa, Australia, America, the East and West Indies, and various parts of the British Empire It is indigenous to America, Asia, and Africa, from whence it was introduced, probably, into other countries. The cotton plant belongs to the natural order Malvaceæ, which includes the mallow and hollyhock. A natural order is subdivided into groups, each of which is termed a "genus" Each genus contains a number of different "species." Cotton belongs to the genus *Gossypium*, which contains several species. The genus *Gossypium* includes herbaceous plants, shrubs, and trees which are naturally perennial Cultivated cotton is, however, grown generally as an annual. The plant produces a flower and subsequently seeds. The latter are covered with hairs whose ultimate function is to assist in the distribution of the ripe seed. These hairs are the raw cotton fibres of commerce. The leaves of the plant are lobate in form, having from three to five lobes.

The flowers (fig 13) are yellow or purple, and grow singly from the axils of the leaves. They have three bracts at their bases each with several indentations, the bracts being joined together at their bases.

The fruit consists of a capsule with from three to five cells (fig. 13A). At first the capsule is closed (fig. 14). It contains the unripe cotton seeds, wrapped in immature cotton hairs. When nearly ripe, the capsule opens and the free ends of the hairs escape, the basal end remaining attached to the seed. Each capsule or pod contains from thirty-two to thirty-six seeds.

Species of Genus Gossypium.—There are a great many different varieties of cotton, and considerable difference of opinion exists as to which are distinct species. The different kinds of cultivated cotton are, however, included in four, or possibly five, species. These are—

1. *Gossypium barbadense.*
2. *Gossypium herbaceum* or *indicum.*
3. *Gossypium peruvianum.*

4. *Gossypium arboreum.*

5. *Gossypium hirsutum*, which is, however, regarded generally as a variety of *Gossypium herbaceum.*

Gossypium barbadense.—This species produces the most valuable cotton, the chief example being "Sea Island" cotton It is characterised by long, fine, silky hairs with an average length of from 1·5 to 2·5 inches. Sea Island cotton is cultivated on the islands and a portion of the mainland of Georgia, South Carolina, and Florida Its special properties are connected with climate, and



FIG. 13.—Twig of American cotton plant.

probably also the saline constituents of the soil, since when grown away from its natural habitat it does not develop them so well. *Gossypium barbadense* is a herbaceous plant or shrub, of from 6 to 12 feet in height, producing a yellow flower and small black smooth seeds, from which the cotton is easily detached. Egyptian and many varieties of American cotton are derived also from *Gossypium barbadense*, although the length and silkiness of the hairs are inferior to that of the Sea Island product.

Gossypium herbaceum is widely distributed, but is indigenous to Asia. It produces most of the Indian and Asiatic cotton, such as Surat, Madras, Tinnevelly. North American cotton, or *Gossypium hirsutum*, belongs to this species, as do, also, some short, low-grade fibres which are, by themselves, of

little textile value. *Gossypium herbaceum* is a shrub which grows to a height of about 4 to 7 feet and produces a yellow flower. The cotton hairs covering the seed have a length of from 0·75 to 1 inch.



FIG. 13A —Large cotton capsules.

Gossypium peruvianum is a South American species. It grows to a height of from 10 to 15 feet, producing a yellow flower and a capsule containing

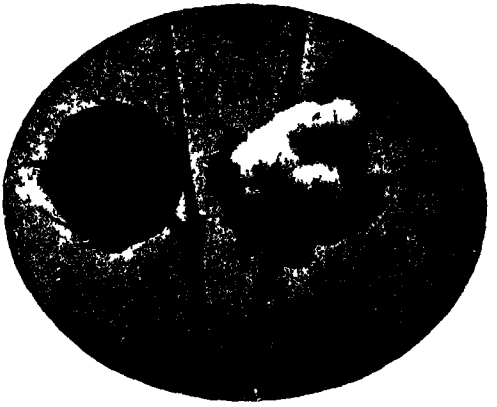


FIG 14 —Capsules of cotton plant.

black seeds, attached together firmly to form a cone-like mass. The hairs are from 1 to 1·5 inch in length. Both Peruvian and Brazilian cottons belong to this species.

Gossypium arboreum grows in India and China. It is a large tree-like

plant with a red flower, producing yellowish-white hairs Varieties of this species are cultivated in the United States of America

Cotton Cultivation.

Although all of the above species of *Gossypium* are perennial, producing yearly crops of cotton, the quality of the fibre deteriorates, after a year or two, even with careful cultivation If the plants are allowed to run wild, this deterioration becomes more rapid and complete The fibres known as "wild" cotton have little commercial value The best results are obtained when the cotton plant is raised freshly, each year, from seeds This has also the further advantage of enabling the grower to improve his product by the introduction of new strains, produced by selective cultivation Constant attention to the details of cultivating and fertilising the soil is necessary to maintain regularity in quality, while many generations of selective cultivation and cross fertilisation are required to develop and stabilise a new variety In the United States of America the ground is ploughed in the early winter and exposed to the action of the air and frost The weathered soil is then broken up and ploughed into furrows 3 or 4 feet apart The seeds are planted in these furrows, at intervals of about 18 inches This sowing takes place in March and April, but, since it is important to avoid late frosts, it may be deferred till May in unfavourable seasons Under suitable conditions the young plants begin to be visible in about ten days when they are thinned out, if necessary, and the ground is carefully weeded The young plants grow rapidly Warm weather and a certain amount of rain are necessary for their best development Excess of rain favours the growth of weeds and causes the cotton plant to produce woody tissue at the expense of the cotton hair Excessive dryness, on the other hand, inhibits the growth of the plant and this causes a small crop of cotton, which ripens too soon While moisture is essential during the earlier stages of growth, after the flowers have opened, warm dry weather is essential to the proper ripening of the crop The flowers open at the beginning of June The blossom is succeeded by the closed pod, which contains the seeds wrapped in unripe, actively growing cotton hairs Later, the pod opens, and the free ends of the cotton hairs escape and expand to a white, fluffy mass This is termed a "boll" The ripening of the hairs, followed by the gradual atrophy and drying up of the cell contents now sets in, and this is the most critical period during the life history of the cotton It is during this time that the thick cell walls and the characteristic twist are produced Any unfavourable conditions such as excess of moisture or deficiency of sunlight, retard or inhibit the ripening process, causing the hairs to have thin walls and to be deficient in natural twist The gradual drying up of the cell contents, under the influence of the sun, is responsible for the production of the twist Young cotton hairs are turgid with cell liquid and devoid of twist The drying of the cell contents proceeds irregularly This causes local contraction and partial collapse of the cell walls These factors produce, in turn, torsion which causes the hair to twist on its longitudinal axis Both deficiency, or excess, of sunlight exercise a prejudicial effect on the drying up of the cell contents Rapid drying, caused by a fierce sun, is not desirable Under such conditions the drying proceeds too quickly and a harsh cotton somewhat deficient in twist results Cottons, such as Sea Island and Egyptian, which mature under the best possible conditions, are characterised by softness, regularity, and highly developed twist The gathering or picking takes place from August till October. The crop is dried in the sun and then "ginned," to remove the cotton from the seeds The latter

constitute nearly two-thirds of the freshly gathered cotton. The "gin" is a machine designed to detach the fibres from the seeds, without damaging either, and to separate them from the seeds at the same time.

There are three types of gins illustrated by (1) the Whitney saw gin, (2) the Macarthy gin, and (3) the knife-roller gin.

The following brief descriptions are taken from Bowman's *Structure of the Cotton Fibre*.—

The Whitney Saw Gin is the oldest form, dating from 1794. It is used largely for American cotton, except in the case of Sea Island It consists of a number of saw-toothed discs forming a cylinder like a number of fine, circular saws, with an interval between each, and threaded on to a revolving shaft, usually of square section The teeth of the circular saws protrude through a grid into a chamber containing the cotton seeds The bars of the grid are just far enough apart to allow the saws to clear The cotton fibre, or lint, is caught up by the teeth of the saws and drawn through the grid. It is then removed from the teeth by means of a revolving brush, and carried away from this by a current of air The seeds, after removal of the lint, fall through an opening in the hopper into a special receptacle They are crushed and pressed to remove as much of the cotton-seed oil as possible The residue is made into cotton-seed cake, which is a valuable cattle food The cotton-seed oil is used for soap-making and other purposes.

The Macarthy Gin.—The saw teeth of the Whitney gin are liable to rupture the cotton hairs unless adjusted very carefully. In the Macarthy gin the teeth are replaced by an adjustable knife The cotton seeds are placed in a hopper, or receptacle, provided with a grid A leather-covered roller revolves close to the grid, the latter having the same width as the roller and forming the bottom of the receptacle or hopper, into which the unlinted seed is fed The seeds are pushed against the roller by a reciprocating feed-bar, and an adjustable "doctor" knife holds back the seeds, while the lint is carried up under it, by the revolution of the rough leather-covered roller, in a continuous film

The Knife-roller Gin.—This consists of either single or double leather rollers, the lint being removed by means of a knife

Ginning is an important process, and if it be carried out improperly the cotton may be damaged. If the fibres are torn from the seed too roughly they may become ruptured, or stretched beyond the limit of their elasticity Sometimes particles of the seed coat are cut away with the hairs This introduces the short, downy hairs, with which the seed is covered, into the lint, and which are difficult to remove subsequently

Cotton treated by a roller gin is much less likely to be damaged than when a saw gin is used, but the damage caused by the latter is compensated for by the greater output obtained. After ginning, the raw cotton is pressed into bales and is ready for the market.

The impurities present in raw cotton are –

1. Bracts and fragments of leaves
2. Small pieces of the seed coat with attached hairs (termed bearded motes)
3. Neps, or small whitish specks, which consist of tangled masses of partly developed or short hairs
4. Sand or other mineral matter
5. Excess of water

In addition to these, "stained" or "boll-stained" cotton, unripe or dead hairs, may also be present. Stained cotton may be due to exposure to frost,

while boll-stained cotton is caused by excessive rain extracting colouring matter from the capsule and bleeding on to the fibres. Unripe, or dead, cotton may be derived from immature bolls or those killed by frost But all bolls may contain a few dead or immature hairs. These will be described more fully later.

All of these impurities detract from the value of the cotton. Their comparative absence, coupled with regularity of the fibres, or staple, with respect to length, fineness, and colour, are the chief factors which decide the actual value of a particular sample

Classification of Commercial Cotton.

The different varieties of cotton are distinguished by certain characteristic physical properties, and by the fineness or count of the yarn which may be spun from them.

In general, cotton is classified by the average length of its staple into fine, medium, and short This is illustrated by the following table taken from the Textile Recorder Year Book 1922 —

CLASSIFICATION OF THE WORLD'S COTTON CROPS

Variety	Where Grown	Length of Staple	Spinning Counts Maximum
		Inches	
GRADE I — FINE			
Sea Island	Charleston, S C	2 and over	300 s
	Florida and Georgia	$1\frac{1}{2}$ $1\frac{1}{4}$	120 s twist
Egyptian (Sakel)	Lower Egypt	$1\frac{1}{4}$ $1\frac{5}{8}$	150 s weft
Pima	Arizona	$1\frac{1}{16}$–$1\frac{5}{8}$	
Sudan	Tokar, Gozna, and Kassala	$1\frac{1}{4}$ $1\frac{1}{2}$	100 s
Egyptian (Uppers)	Upper Egypt	$1\frac{1}{8}$ $1\frac{1}{4}$	
Staple American	Mississippi, South Carolina, etc	$1\frac{1}{16}$–$1\frac{1}{16}$	80 s
Peruvian	Peru	$1\frac{1}{8}$ $1\frac{3}{8}$	
Brazilian (long staple)	Northern Brazil	Up to $1\frac{1}{2}$	
Staple American	Nyasaland, Uganda, East and South Africa, Mesopotamia, and Queensland	$1\frac{1}{8}$ $1\frac{1}{4}$	60 s
GRADE II — MEDIUM			
American	U S A	$\frac{7}{8}$ $1\frac{1}{8}$	
	Mexico	$\frac{3}{4}$ $1\frac{1}{8}$	
	Brazil	$\frac{3}{4}$ $1\frac{1}{8}$	
	Russia	1 $1\frac{1}{8}$	40 s
	West Africa	$\frac{3}{4}$ $1\frac{1}{8}$	
	Levant	$\frac{3}{4}$–$1\frac{1}{8}$	
	India	$\frac{7}{8}$ 1	
	China and Corea	$\frac{3}{4}$–1	
GRADE III — SHORT			
Chinese	China, etc	$\frac{3}{8}$–$\frac{3}{4}$	30's

A few typical cottons may be referred to briefly

Sea Island Cotton.—This is the highest type of cotton and the most valuable. It grows on the coast of the Gulf of Florida, and in the Barbadoes and other islands where the soil and climate are especially favourable to cotton cultivation.

Sea Island cotton is characterised by a long fibre, its average length being over 2 inches. It is, of course, correspondingly fine, and can therefore be spun into the finest counts up to 300's. The fibre is very regular, has a highly developed natural twist and a small proportion of unripe hairs Compared with other cottons, it has a high lustre and a soft, silky feel Its colour varies from cream to white. There are many varieties such as Florida, Queensland, Fiji.

Egyptian cotton is of two kinds, viz brown and white The brown variety is finer than the white. Like Sea Island cotton, it is very regular in quality and fully matured. The brown colour varies in depth It is easily removed by bleaching, but it makes it difficult to mix the cotton with other varieties in its unbleached state It is the next finest cotton to Sea Island, the length of its staple averaging from $1\frac{1}{2}$ to $1\frac{3}{4}$ inches It is used for fine counts and can be spun up to 200's White Egyptian cotton is not so fine as the brown variety, being not much more than an inch in length

South American cotton has a medium length of staple, varying from 1 inch in the lower to $1\frac{1}{2}$ inches in the higher grades It is strong, but irregular in quality, and often has a harsh feel This is due, probably, to the rapid drying of the cell contents after ripening. It cannot be used alone for fine counts, its maximum spinning power being about 70's

American cotton, grown in the United States, is represented by a large number of varieties, produced by selective cultivation Some of these, such as Peeler, Bender, and Allanseed, have an average staple of 1 to $1\frac{1}{4}$ inches, and are used for medium fine counts such as 80's The lower grades, such as St Louis cotton, average 0·9 inch in length, and are used chiefly for low counts such as 32's American cotton is characterised by its good colour, cleanness, and, except in bad seasons, regularity of staple

Indian cotton has a comparatively short hair of from 0·6 to 0·8 inch. It is somewhat harsh, and contains a considerable quantity of mineral matter compared with other varieties It has little spinning power.

China cotton is a good example of a low-grade variety. The hairs average from 0 5 to 0·7 of an inch in length and are correspondingly coarse They are also harsh, and the twist is not highly developed China cotton has low spinning power, and is of comparatively little use except for mixing with higher grade cotton

The following table gives a summary of the comparative qualities of these varieties –

Origin of Cotton	Length of Fibre.	Diameter in Inches.	Spinning Power
Sea Island	2 and over	1/1500	300
Egyptian	$1\frac{1}{2}$–$1\frac{3}{4}$	1/1500	200
South American	1 –$1\frac{1}{2}$	1/1300	70
American	0 9–$1\frac{1}{4}$	1/1300	70
Indian	0 6–0 8	1/1200	
Chinese	0 5–0 7	1/1200	

Blending.—Many yarns are made from blends of two or more different varieties of cotton. By careful blending, the properties of two or more kinds can be made use of to supplement each other, to lessen the cost of manufacture, or to make a yarn suitable for producing particular effects in a fabric. "Twists,"

or yarns designated for warps, can only be made from the higher grades of cotton, since they must have a high tensile strength and elasticity Weft yarns can be spun from lower grades, for, in these, strength and elasticity are not so essential, fullness of body being the chief requirement

Each variety of cotton is divided into certain grades which are recognised by buyers and sellers These are designated by the initial letters of the descriptive terms

Thus American cotton is graded as—

1 Good Ordinary or G O
2 Low Middling or L M
3 Middling or Md
4 Good Middling or G M
5 Fully Good Middling or F G M
6 Middling Fair or M F

Good Ordinary is the lowest and *Middling Fair* the highest type The grades of other varieties are designated differently but each is recognised and quoted at a different price

Hird (*J Text Inst*, 1923, P 269) gives the following description of the grade of raw cotton —

'The grade of raw cotton, strictly speaking, depends on its colour and the amount of leaf, stalk, and particles of broken boll that it contains The staple of raw cotton, strictly speaking, is the length of the individual fibres The selection of cotton is the determination of these two characteristics, and the arranging of the cotton into uniform or even running groups A spinning mill which requires a certain grade of cotton must have that grade, or at any rate approximately that grade and the same applies to staple A merchant who offers a mixed lot of cotton is fortunate if he gets the price of the lowest grade bale for the whole lot Every bale in a well selected lot of 100 bales must be of the same grade and the same staple as every other bale There are, however, more characteristics to be looked for than those described in the bare definitions of grade and staple, bales of the same colour, and containing the same of leaf or trash, may differ through one being well ginned and another gin-cut and full of nep Another may contain too much moisture, giving it a dead, flat appearance, and another, not very frequently met with, may be impregnated with fine sand

In deciding the staple of cotton, there are still more points to be considered beyond the bare length of the fibre Fineness is an important consideration, a mill using a fine, long stapled cotton would be unable to use a coarse cotton even though the fibres were of the same length Evenness is of the highest importance, since if some fibres are appreciably longer than others in the same bales, the rollers must be adjusted to take either the longer or the shorter, if the former, then the shorter fibres will fall out and there will be a large amount of waste, and if the latter, faults will appear in the yarn Strength is another thing to look for, and often differs materially, even between bales grown in the same district Raw cotton is sampled, roughly, by taking a little and pulling it out carefully with the finger and thumb of both hands The length of the fibres and their resistance to breaking tension are noted The sample is then examined for motes, neps, bracts, dirt, and colour "

Cotton Buying.—Cotton is generally bought, in England, through a broker It may be either (1) "spot" cotton, (2) "on call" cotton, or (3) cotton "futures" Spot cotton is, as the term denotes, actually on the spot, and can be examined

before buying and delivered at once, and must also be paid for. Sometimes a buyer does not want a large quantity of cotton, immediately, but still wishes to secure a supply of a particular grade every fortnight or month. For this purpose, he places a contract with a broker for the delivery of a certain number of bales, as required, at the price ruling at the time of actual delivery. This cotton is said to be on call. Cotton futures is the term applied to cotton on call, except that the period may be longer and the quantities involved greater. Cotton futures often become a form of gambling on the price of cotton, say three or six months hence.

Cotton Spinning.—Silk is the only textile fibre which can be used for weaving into fabrics in its raw state. All others must first be spun into yarns. In the case of cotton, spinning may be defined as the process of arranging the fibres parallel to one another and then twisting them round a continuous longitudinal axis The threads thus produced may be doubled together and again twisted, to produce two- or three-fold yarns

The number of fibres in a cross section depends upon the diameter of the fibre and the "count" of the yarn The finer the fibre, the more fibres are required to make a yarn of a given count or diameter. The following table, given by Bowman (*The Structure of the Cotton Fibre*, p 365), illustrates this point —

Counts	Average Number of Fibres in Cross-section of Thread	
	American Cotton	Egyptian Cotton
40's	120	161
50's	92	129
40's twofold	225	320
50's twofold	180	240

The number of complete turns per inch of twist depends upon the kind of cotton, the count of the yarn, and its intended use. The usual number is determined by multiplying the square root of the count by a factor. For warp yarns this varies from 3·75 to 4·25, while in the case of wefts it is from 3·25 to 3·50

Spinning.—Raw cotton, as it comes from the bale, consists of innumerable fibres pointing in all directions In order to spin these into yarn two operations are essential (1) to draw out continuously uniform quantities of the fibres, in such a way as to make them lie approximately parallel to one another, and (2) to twist these fibres together, to form a continuous thread. In early times this was accomplished by means of the spindle and distaff. The latter was a stick to which a bundle of the fibre was attached loosely, the distaff being either held in the left hand or fastened in the belt of the spinner. The spindle was a small, tapering rod, the rotation of which gave the twist to the fibres, and around which the twisted thread was wound The twist was imparted by rotating the spindle against the body with the right hand and then letting it, whilst still rotating, fall to the ground During its fall, the spindle further drew out the fibres and, at the same time, twisted them together In order to increase the momentum of the fall, the spindle was weighted with a stone or metal whorl, till the weight of the yarn wound on it was sufficient for the purpose The spindle and whorl

are illustrated in fig. 15, taken from Chambers's *Encyclopædia*, from which much of the information given is also derived.

An early improvement on the original distaff and spindle was the provision of bearings for the spindle, and a belt and wheel to produce rotation. A special bobbin was also added upon which the yarn was wound as it was spun Still later, a treadle was introduced which enabled the spindle to be rotated continuously, and allowed the use of both hands. This was known as the Saxon wheel (fig 16)

A further improvement upon this consisted of placing on the spindle a bobbin with a separate motion and provided with two bent arms, termed the flyer, or flight, for winding the yarn on the bobbin The bobbin and flyer revolved at different rates, the former imparting the twist and the difference in the rates of rotation causing the winding of the yarn.



Fig 15.—Spindle and whorl

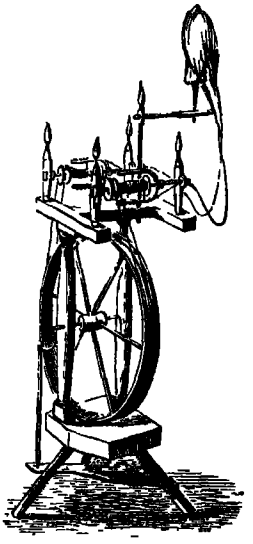


Fig 16.—Saxon wheel

Purely mechanical spinning was not invented till 1764, when the spinning jenny was invented by Hargreaves Since that time great developments have been made, though the essential principles remain the same as those of the distaff and spindle The processes may be divided into (1) preliminary or preparatory processes The object of these is to open out the fibre, remove short hairs and extraneous matter, lay the fibres approximately parallel to one another, and then pull them out in a continuous round rope, or strand, of uniform diameter, termed a sliver, and, finally, to draw out or attenuate the sliver till it contains the desired number of fibres in its cross-section (2) Spinning or twisting together this attenuated strand

The raw cotton is first passed through a machine termed an "opener" This consists of cylinders studded with teeth and revolving at a high speed, which tease the cotton into separate fibres and form a uniform mass termed a lap (fig 17). At the same time the dust, and other extraneous matter, are removed by means of a current of air.

From the opening machine, the cotton passes to the "scutcher," which is of

a similar nature The fibres are again teased out and a broad, uniform lap is produced The lap goes to the "carding machine." This consists of a number of cylinders which are covered with wire teeth bent at right angles. The cylinders vary in diameter, and can be rotated at different velocities and in the same or in opposite directions. The direction and rate of rotation determine whether the points of the wire teeth, or their flat sides, meet one another or pass. Thus, some of the cylinders remove the fibre from one and pass it on to another, ensuring that it shall be teased out thoroughly and spread in a uniform manner. The broad lap leaves the carding machine through a ring, which converts it into a round rope or sliver. The short fibres are also removed by the carding machine, so that the sliver consists of those of approximately uniform length. For the



FIG. 17.—Lap of cotton.

finest yarns the sliver is submitted to a process termed "combing," which produces still greater uniformity of length. Fig. 18, taken from Hannan's *Textile Fibres of Commerce*, illustrates a combed sliver.

The next operation is "drawing out." The sliver is passed through a "drawing frame." This consists of successive pairs of rollers, each pair revolving more rapidly than that preceding it This causes the sliver to become drawn out or attenuated, and makes the fibres more nearly parallel to one another. The amount of the drawing out depends upon the relation between the rates of rotation of the initial and final pair of cylinders. If, for example, the final be six times that of the initial rate, the sliver is drawn out to six times its original length, or six are made into one of the same thickness as each of the original slivers The process is repeated, if necessary, till sufficient drawing-out is obtained. This drawn-out sliver is then passed through a "slubbing frame," where it is drawn out still further and given, at the same time, a slight twist, which enables it to be wound on a bobbin. The product of the slubbing frame

is termed a "slubbing." Two slubbings are then drawn out together, to the thickness of one, again slightly twisted, and wound on a bobbin by an "intermediate frame" After the intermediate frame comes the "roving frame," which attenuates, again slightly twists, and winds the "roving" on to bobbins These rovings are then spun. Spinning may be either continuous or intermittent. The former is done by the "throstle," the latter by the "mule," spinning frame Throstle spinning is used for coarse yarns and the mule chiefly for fine counts Throstle spinning is similar in principle to the spinning-wheel. Spinning is continuous, and the yarn is wound on to the bobbin as it is spun. The apparatus consists of a



Fig 18.—Cotton sliver

spindle, bobbin, and traveller The spindle and bobbin, revolving together, produce the twist The yarn passes to the bobbin through a traveller, or eye of steel, set on a flanged steel ring, which encompasses the spindle and bobbin The traveller keeps the yarn free from the bobbin while the twist is being put in, and, being carried round by the bobbin, it winds the yarn on to the latter The filling of the bobbin is regulated by an up-and-down motion, communicated to the rail on which the ring and traveller are fastened Mule spinning is intermittent. The bobbins carrying the rovings are mounted on a fixed frame Yarn bobbins or cops are attached to the spindles, which are mounted on a carriage which can travel backwards or forwards over a space of a couple of yards The frame carries, also, drawing rollers, which give out fixed lengths of the rovings. As they begin to do this the carriage moves backwards and the spindles simultaneously rotate Thus, the roving is drawn out and spun at the same time When

the carriage has completed its backward movement, the drawn-out roving is spun. The carriage then travels back to the frame, during which time the yarn

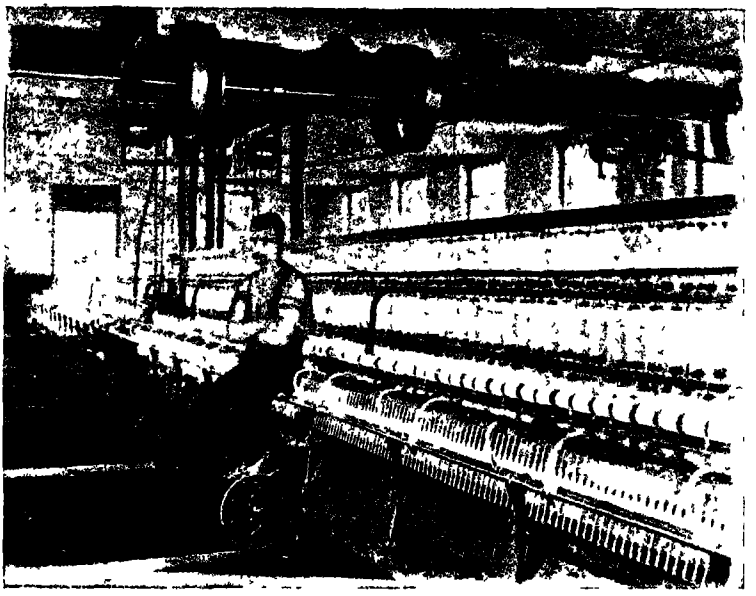


FIG 19 —Mule spinning frame

is wound on to the rotating bobbins or cops The process is then repeated indefinitely. Fig 19 illustrates a mule spinning frame

CHAPTER IV

VEGETABLE CELLS.

EACH cotton hair is a single complete vegetable cell which, after reaching maturity, gradually dries up and partially collapses A living vegetable cell consists of the following parts, which may be seen in fig 20, taken from Vines' *Text Book of Botany* —

1 A cell wall or limiting membrane which consists generally of cellulose
2 Protoplasm
3 A cell cavity or cavities generally termed vacuoles
4 Cell sap, which permeates the protoplasm and fills the vacuoles

The protoplasm is the essential constituent of all living cells It is a jelly like nitrogenous substance of a very complex nature giving the reactions of proteins A portion of it is generally differentiated into a ' nucleus," in which are one or more smaller " nucleoli ' These consist of a specialised kind of protoplasm The nucleus performs some definite function in the life of the cell, and, as a rule, division of the cell protoplasm is preceded by that of the nucleus In a young cell the cell cavity is entirely filled with protoplasm (fig. 20, A) As the cell increases in size, the growth of the protoplasm does not keep pace with that of the cell wall It adheres to the cell wall, but owing to its extension vacuoles make their appearance (fig 20, B), which are filled with cell sap As the cell continues to grow, the vacuoles increase in size till ultimately they constitute the greater part of the cell Sometimes there is only a single vacuole, as in fig 20, C, or several as in fig 20 D

While the cell is growing, it is always full of cell liquid and turgid But after reaching maturity, growth ceases and, frequently, the cell contents atrophy and dry up, leaving an empty cell cavity This is the case with the cotton hair The size and shape of a single cell is very variable. The smallest may be spherical and not measure more than 0 001 of a millimetre in diameter, while a single cotton hair may reach a length of from 2 to 3 inches The cell wall is produced and laid down by the protoplasm A young cell may consist entirely of proto plasm which soon secretes a thin envelope of cellulose As growth proceeds, the protoplasm, which is always attached to the wall in a living cell, lays down successive layers of cellulose upon the interior surface of the cell Thus the cell wall has a stratified formation, though this is not always readily seen While the cotton hair is a single specialised cell, the tissues of plants consist of collections of cells joined or cemented together The cell walls of these may be adapted to the special purpose for which the tissue is required Thus, they may be lignified in the case of woody tissues or cuticularised in the case of cork cells Besides living protoplasm and cell sap, vegetable cells may contain other bodies for special purposes. These include starch grains, proteins, fat, or wax, and crystals of mineral salts The cell sap is an aqueous solution of various soluble

sodium and potassium salts of both inorganic and organic acids. Among the salts present are nitrates, phosphates, and sulphates. Organic acids, such as citric and malic acids, may be present either as salts or in the free state. Soluble amino compounds, such as asparagin, are also found, and often sugar, colouring matters, tannins, and glucosides.

The cotton hair, when young and actively growing, is a long, tapering cylindrical cell attached to the seed at its basal end and completely filled with protoplasm and cell liquid Later, as the growth of the cell outstrips that of the

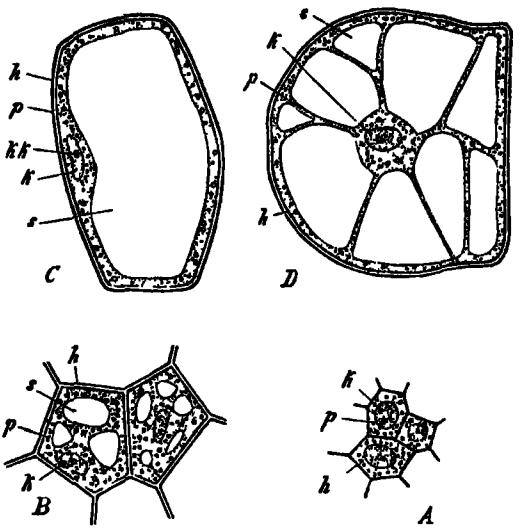


Fig 20 - Vegetable cell

A, Young cells from the ovary of *Symphoricarpus racemosus* × 300 , B, cells from an older ovary of the same plant × 300 , C and D from the fruit of the same plant × 100 , *h*, cell wall , *p*, protoplasm , *k*, nucleus , *kk*, nucleolus , *s*, vacuole In C there is a single large vacuole, the whole of the protoplasm forming the parietal layer In D there are several vacuoles, and the nucleus lies in a central mass of protoplasm connected with the parietal layer by numerous strands

protoplasm, the latter becomes collected round the cell walls and a vacuole or cell cavity is formed When growth has ceased, the protoplasm and cell sap dry up gradually, leaving a partly collapsed cell cavity containing these dried-up remains A well-matured and dried-up cotton fibre thus consists of—

1 The cell wall composed of layers of cellulose together with similar bodies, such as pectose.

2. The dried-up protoplasm.

3 The substances which were dissolved in the cell sap, such as salts, amino compounds, and colouring matters.

4. Substances secreted by the protoplasm for special purposes, such as cotton, oil, or wax

5. Water.

CHAPTER V.

THE STRUCTURE OF THE COTTON HAIR; VARIATIONS IN STRUCTURE—UNRIPE, DEAD, AND ABNORMAL HAIRS.

SINCE each cotton fibre or hair is a single complete cell, its microscopic structure will be, in general, similar to that of the typical cell described in the last chapter. The length of the hair varies with the kind of cotton and its position on the seed Those growing near the base are short in comparison with the others. The hairs on a cotton seed may generally, according to Bowman (*Structure of the Cotton Fibre*, p 110), be divided into four classes, which, however, are not very distinctly defined. These are—

1. Short, stumpy, stiff fibres, usually found near the growing point of the seed, and which are the last to develop These are termed basal fibres They are too short to spin, and are generally left on the seed by the gin

2 Immature or unripe fibres, in which no internal structure can be seen

3 Tubular fibres with a distinctly marked lumen or cell cavity, and well-defined cell walls exhibiting the characteristic twist

4 Fibres whose structure is tubular, and in which the cell wall with its secondary deposits almost fill the cell cavity, giving the fibre a dense and opaque appearance These fibres exhibit the characteristic twist to a marked degree

Short fibres form an undergrowth to the longer ones They are, as stated above, left behind by the gin But if fragments of the seed are taken off by the gin, these short fibres are incorporated with the cotton, and if not removed produce neps They may, however, be removed from the seed by means of a special machine, and are used for making blotting-paper . Immature or unripe fibres are present, to a certain extent, in all raw cotton The number varies with the conditions of cultivation Bad seasons, with little sun, increase the percentage, and a similar effect may be produced by leaving the cotton ungathered after it has fully matured. Bowman distinguishes another form of immature fibre, in which the cell is, in places, transformed into a non-porous state, impervious to dye liquors This condition is observed, generally, near the upper end of the hair It is accompanied, not only by imperviousness to liquids, but also by brittleness, the latter causing the tip of the fibre to break off during manufacture These hairs are very similar to "kempy" fibres in wool

They are found only in coarse varieties of cotton, and not in those of a high grade such as Egyptian or Sea Island Classes 3 and 4 include all the hairs which are nearly or fully matured and which form the bulk of raw cotton A typical cotton hair consists of four distinct parts, which may be seen in fig 21, which represents a longitudinal section by De Mosenthal. These are—

1. An outer coat or cuticle.
2 The cell wall.
3 The inner cuticle lining the cell cavity.
4 The cell cavity, or lumen, containing the residual dried-up protoplasm and cell liquid.

The cuticles are composed of a differentiated kind of cellulose termed "cuticular cellulose," which offers considerable resistance to the action of solvents which dissolve the cell walls readily. The cell walls, which constitute about 90 per cent. of the hair, consist of normal cotton cellulose. If a complete cotton hair be



Fig 21.—Longitudinal section of cotton hair

examined under the microscope, it is seen to have an open basal end where it was cut from the seed, and to taper, gradually, to a point at its free or upper extremity Numerous spiral twists or convolutions can be observed throughout its length (fig 22) which may be either right-handed or left-handed in direction

These convolutions are peculiar to cultivated cotton, and are an important factor in determining its value as a textile fibre. They are developed, chiefly, after the hairs have escaped from the pod, and are caused by the uneven drying up of the cell wall and cell contents Bowman (*loc cit.*) gives the following explanation of the process The parts of which the fibre is composed differ in structure and density. The cell wall formed by the secondary deposits is not of equal thickness throughout, and the drying up takes place first where the cell wall is thinnest This produces a strain on the cell wall, and as the thinner portion collapses it tends to cause the cell to twist round its central axis This occurs in different portions of the hair simultaneously, but specially where it is directly exposed to the action of the sun The number of convolutions in a single hair may vary from 200 in the case of a coarse Indian to 400 for a fine Sea Island cotton Bowman states that the number of convolutions per inch depends upon the fineness or variety of the cotton, and gives the following table (*Structure of the Cotton Fibre*, p 118) · —

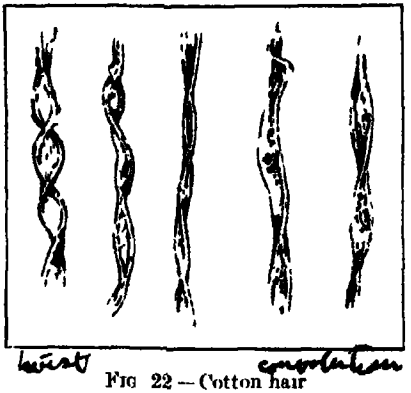


Fig 22 — Cotton hair

	No tested	Maximum	Minimum	Mean
Sea Island .	50	360	240	300
Egyptian	50	280	175	228
Brazilian . .	50	260	158	210
American (Orleans)	50	240	144	192
Indian (Surat)	50	190	120	150

This is not, however, confirmed by the work of Gladys G. Clegg and Harland, who have made a very exhaustive study of the subject (*J. Text. Inst.*, 1924, T. 14).

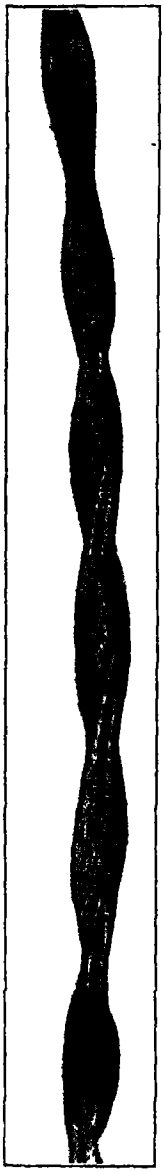


Fig 23.—Surface of cotton hair showing convolutions

These authors found that the number of convolutions in any portion of a single hair depends upon the ratio between "ribbon width" to wall thickness. The highest number, per field, is shown when this ratio has the value 3·4 to 3·6. They observed, further, that wetting of the hair causes a partial elimination of the convolutions and of the reversals, but, on redrying, both convolutions and reversals return almost unmodified to their original positions. Boiling the hairs, under pressure, causes an almost complete disappearance of both convolutions and reversals, accompanied by much swelling, but, on redrying, they reappear Tension causes the pulling out of some of the convolutions, but the reversals remain unaffected When the tension is released there is a distinct tendency for the hair to resume its original form.

The distribution of the convolutions was mapped by Clegg and Harland in the form of curves for a number of different cottons They found that, in the case of six cottons out of seven, the curve is a two-peaked one, with a wide valley occurring somewhere in the middle of the hair, and they concluded that the form of curve is "predetermined" by environmental conditions prevailing during the period of growth of the hair That is, the distribution of the convolutions are not entirely accidental, as suggested by Bowman. No differences in the number of convolutions or reversals per millimetre exist which are capable of producing much effect on spinning quality, but the degree of uniformity of distribution of reversals may be an important factor. With regard to this, they note that there does not appear to be any scientific foundation for the practice of judging the degree of natural twist in a sample of raw cotton by pulling a handful apart and watching the rotation of the individual hairs

With regard to the occurrence of convolutions at predetermined positions on the hair, Denham (*J Text Inst*, 1923, T 94) makes the following observation "The cotton hair is commonly described, in the popular literature, as a long, straight evenly built tube of cellulose, which flattens and twists upon the death and desiccation of the cell This conception is fallacious The hair grows in a closed boll, and the space available for its development is very small compared with the length to which the hair can grow. Consequently, the hair is compelled to double back upon itself several times, with more or less sharp bends, and these bends are fixed in the hair structure by the ensuing secondary thickness of the wall A single hair, drawn from a ripe seed, will fall into a pattern, in some degree reproducing the position in which it grew, and a certain amount of force is needed to keep the hair stretched in a straight line. A number of the convolutions on a hair, when carefully examined,

will be found to consist of these bends more or less deformed, according to the amount of straightening which they have undergone since." The convolutions, according to Denham, follow the direction of the primary wall striations, and are caused by a double spiral line of weakness

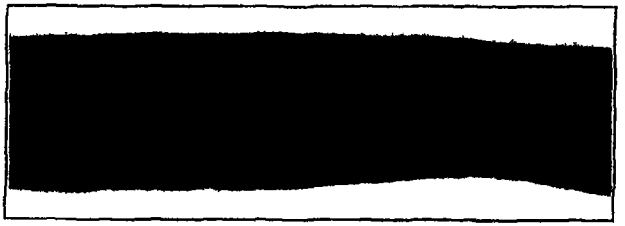


FIG 24.—Cotton hair showing spores.

Fig 23, taken from a paper by De Mosenthal (*J S C.I*, 1904, p. 293), illustrates the superficial appearance of the convolutions on a cotton fibre.

The surface of the hair appears to be striated, corrugated, or indented. De Mosenthal (*loc. cit*) thinks that many of these markings can, with proper preparation of the slides and high magnification, be resolved into pores and rows of stomata These are illustrated in fig. 24

These structures cannot, however, be stomata in the true botanical sense A stoma always consists of at least two cells, and is often multicellular Denham, for these reasons, terms them "bearded pits" There are present, also, striations and corrugations which cannot be resolved into rows of bearded pits He states that "comparison of both of these structures with the *Verschiebungen* found in such fibres as flax and hemp led to the suggestion that they were due to the same cause as the latter, and were of the nature of 'slip planes,' such as those described by Robinson in aeroplane timbers These slip planes are probably produced by longitudinal (crushing) and lateral (shearing) stresses" They are illustrated in fig 25[1] from Denham's paper in the *Journal of the Textile Institute* (*loc cit*)

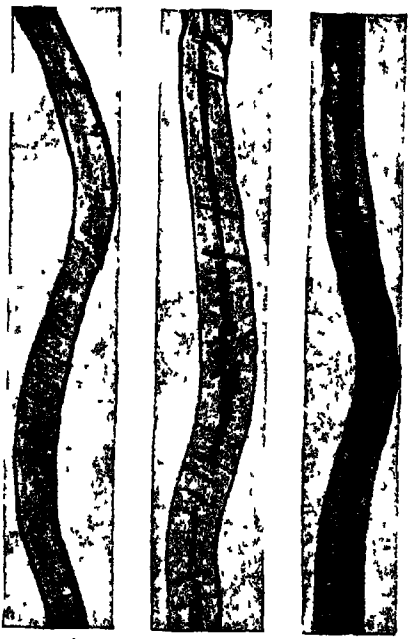


FIG. 25.—Slip planes.

Others of the surface markings are due, according to Denham, to "buckling" The surface of the fibre has a granular appearance suggesting striations beneath. These striations occur in all parts of the hair It was found by Denham that convolutions follow the direction of the primary wall striations. These are not

[1] Illustration by courtesy of the British Cotton Industry Research Association.

always visible in an untreated hair, but become plainer after treatment with a swelling agent such as sulphuric acid and iodine Many illustrations of these striations are given in the original paper, which should be consulted

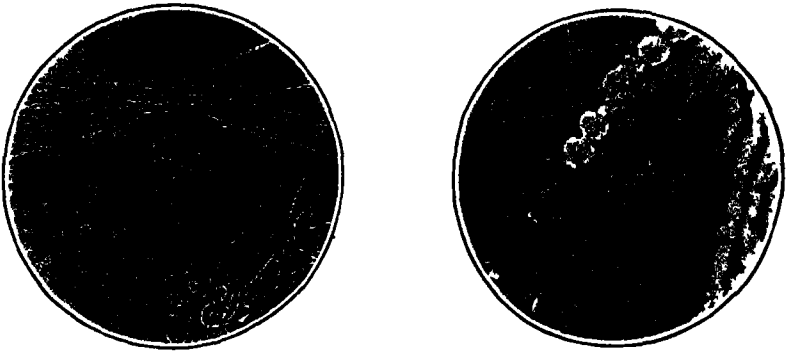


FIG. 26

A Low power B. High power

The cuticle of the cotton hair is not easy to distinguish from the cell walls without preliminary treatment It consists, as stated above, of a more resistant type of cellulose than the latter When a cotton hair is treated with a cellulose solvent, the cell walls swell up and finally dissolve before the cuticle is attacked



FIG 27 —Fragment of cotton cuticle

This swelling of the cell walls causes the rupture of the cuticle and the protrusion of globular swellings of partly dissolved cell-wall cellulose These swellings are separated by constrictions, where the ruptured cuticle can be seen wrapped round the hair. The inner cuticle lining the cell cavity can be seen also. These globular swellings are illustrated in fig. 26.

The superficial appearance of a fragment of cuticle from cuprammonium

solution is illustrated in fig. 27, taken from De Mosenthal's paper already referred to.

Schweitzer's solution may be used for this experiment Fleming and Thaysen (*Biochem J*, 1920, p. 25, 1921, p. 407) recommend the following method of examining the cuticle From 0·1 to 0·3 gramme of the sample is boiled with 1 per cent sodium hydroxide solution, soured in acetic acid, washed and steeped in 1·5 c c of 15 per cent sodium-hydroxide solution, followed by the addition of 1·5 c.c. of carbon bisulphide. After from fifteen to forty-five minutes some of the fibres are placed on a slide, covered with a cover slip, and a drop of water allowed to diffuse underneath the latter

The cell wall consists of layers of cellulose laid down, successively, by the living protoplasm of the cell The thickness of the wall varies, as noted above, with the degree of maturity of the hair, and is the chief factor in determining its textile value The cellulose of the cell wall is differentiated from that of the cuticle by being more readily soluble in solvents such as Schweitzer's reagent This does not, however, imply that it is a different chemical substance According to Harrison (*Trans Nat Assoc Cotton Mnfrs*, 1916, pp 101, 198), it is probable that the difference between the cellulose of the cuticle and that of the cell wall is not of a chemical nature but one of colloidal condition, the outer being more solid than the inner portions The laminated structure of the cell wall is seen in fig 28, which represents a longitudinal section of a cotton hair by Bowman.

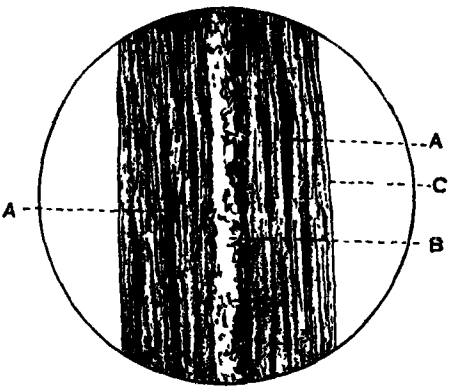


FIG 28.—Cell wall of cotton hair
(From Bowman's *Structure of the Cotton Fibre*)

Cotton depolarises and shows brilliant colours when examined by polarised light, which indicates differences in the physical condition of the different layers of the cell wall De Mosenthal observed that precipitates of cotton and nitrated cotton from filtered solutions do not depolarise The differences of appearance in polarised light observed, when the cotton fibre is treated in various ways, including nitration, must be, no doubt, ascribed primarily to a change in the relative tension or strain of the layers The different layers of cellulose in the cell wall are, according to De Mosenthal, made up of minute spherical granules of nearly uniform size (about 1 μ) They lie closely packed, kept in position by the outer and inner cuticles, and it is only when the tension of these is sufficiently relaxed that they can escape But beyond this there is some definite plan of arrangement. Bowman (*Structure of the Cotton Fibre*, p 103) was able to make out, in certain cases, a spiral-like arrangement of these secondary deposits. Hohnel described them as consisting of long continuous threads which became straightened when the outer sheath was dissolved and the inner deposit liberated According to W. L Ball, the full diameter of the hair is reached almost at once when its length is only 0 1 millimetre, while its length increases till the twenty-fifth day of development, after which the walls begin to thicken and give strength to the hair The thickening is not uniform but leaves simple pits in the wall, set obliquely, and the closure of these pits when the wall dries, after the boll

opens, gives twist to the fibre. The uninucleate cell contents remain alive until the boll begins to open, when they die from desiccation. "The cell wall is extremely thin for the first three weeks, and the cuticle which covers it can scarcely be differentiated unless the wall has been swollen by Schweitzer's reagent."

Denham (*J Text Inst*, 1923, T 89) has shown that, by treatment with suitable swelling agents, striations may be made to appear in all parts of the cotton hair These have been referred to above While the paper itself should be consulted, the following conclusions may be quoted —

"(*a*) Striation of the primary wall invariably occurs, and where not visible in the untreated hair can be revealed by treatment with a suitable swelling reagent.

"(*b*) Striation of the secondary layers does not necessarily follow the lines of the primary wall, but may occur in any degree of obliquity in each layer.

"(*c*) Where the striations in separate layers follow the same lines they become more and more marked, where they follow different lines the general effect is to neutralise each other

"(*d*) Such striations do not follow constant lines Any one set may alter its direction independently of others, and reversals are frequent

"(*e*) Between individual striations occur lines of weakness, and these break down under treatment with swelling reagents

"(*f*) In many cases there are to be seen two well-marked lines of weakness running parallel with the striations, and separating them into two almost equal bands These are most noticeable when they occur as a double spiral"

De Mosenthal or "bearded pits" mentioned above (*loc cit*) are a special form of slip plane involving distortion of longitudinal striations with or without fissuring of the surface between the striations No true pits exist in the cell wall, but areas of marked permeability occur in a double spiral pattern Denham suggests that the striations are of the nature of "stream marks" caused by the movement of the cytoplasm of the growing cell He deduces from the study of the *Tradescantia* hair and of the cotton hair that the cytoplasm rotates in a double spiral band, adjacent bands moving in opposite directions Striations occur along these lines and the double line of weakness at the junction of the bands.

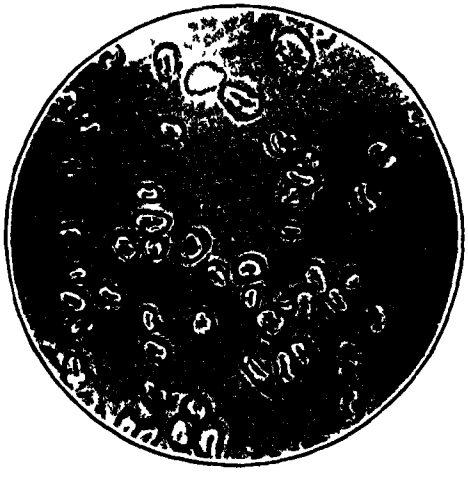


Fig 29.—Cotton hair, cross-section

The inner cuticular layer, like the outer cuticle, consists of a physically modified kind of cellulose which is less readily dissolved than that of the cell walls.

The lumen or cell cavity is irregular in shape, and contains the dried-up protoplasmic remains.

The four essential parts of the cotton hair can be seen in fig. 21. They are visible also in cross-sections, which are illustrated in fig. 29.

Variation in Structure of Cotton Hairs.—It will be noted that the cross-sections of a number of cotton hairs vary considerably in appearance. In some, the cell walls are thick and the lumen plainly visible. In others, the cell wall is thin or even absent, and the lumen indistinct or collapsed. The same differences are noticeable when a number of hairs are examined longitudinally In most cases the secondary layers of the cell wall are very plain, the twist well marked, and the lumen distinct In others, these are not so apparent, while, sometimes, hairs may be seen which resemble a slightly twisted piece of tape. The last two types constitute what are known as "unripe" or "dead" cotton.

Hubner and Pope (*J.S.C.I.*, 1904, p. 404) describe a cotton hair as having the appearance of a flattened ribbon, the edges of which are somewhat thickened and usually slightly turned up, sometimes to such an extent that they stand nearly at right angles to the surface of the ribbon. This description is not in agreement with the facts quoted above, but nevertheless the thickened edges of the hair, even though they may be incorrectly described, are very typical of fully matured hairs and their absence indicative of unripeness. In fig. 30 are shown a number of cotton hairs of varying degrees of ripeness.

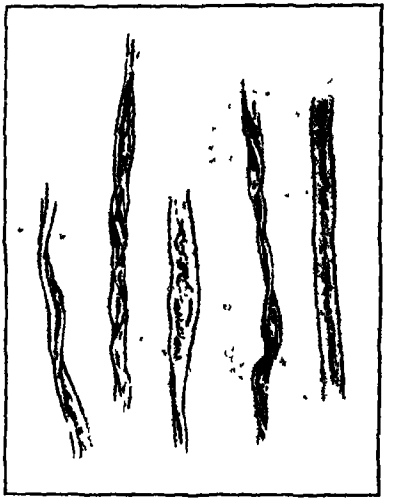


Fig 30.—Ripe and unripe hairs.

The ripening of the cotton depends upon many factors both controllable and uncontrollable Some, such as good soil, the use of fertilisers, absence of overcrowding and of weeds, can be controlled by the grower; others, such as weather, cannot Under favourable conditions the bulk of the hairs will ripen fully, but a small proportion of unripe or even dead hairs is always present. The quantity, however, is inconsiderable and does not exceed 1 per cent But if conditions are unfavourable the proportion may be comparatively large. In such cases the cotton is deficient in tensile strength, elasticity, and spinning power. Moreover, the thin-walled fibres have little resistance to bending stresses Thus they tend to become rolled up together and form neps.

Motes are closely associated with these neps. They consist of (1) a nep which is loosely incorporated in the yarn and becomes detached after printing, leaving a white area below; (2) a loose end of yarn which has become detached or removed to one side after printing, exposing a white patch beneath, (3) small white specks involving a large number of hairs all of which are dyed normally at other portions of their length. Specks of this type are confined to a single strand of yarn, thus eliminating roller damage as a factor in their causation Sometimes the white spots are so far below the general level of the fabric that they could not have been effected by the printing roller. In other cases the mote may be at the general level of the fabric, and possibly protected from the action of the dye by a particle of foreign matter. Streaks, a defect in dyeing, are often shown, confined to a single strand of cotton.

Both motes and neps are, of course, associated, often, with fragments of the seed coat removed in ginning. But, as mentioned above, all cotton contains a

certain quantity of thin walled hairs According to Gladys G Clegg and Harland (*J Text Inst*, 1923, T 125), these are more common in fine cottons, which have naturally a comparatively thin cell wall, than in coarser varieties They may be ascribed to unfavourable conditions of nutrition during growth, while yellowness of thin-walled hairs is invariably caused by the attack of insect or cryptogamic parasites during boll development If thin walled hairs are present, their natural liability to form neps is increased by such processes as ginning, scutching, and carding, and especially by small faults in these Not only are these thin-walled hairs a source of tensile weakness in cotton yarns, but are the cause of trouble in dyeing, since they give rise to light-coloured spots or streaks This appears to be due to a decreased affinity for dyestuffs When dyed with direct dyestuffs, unripe hairs acquire a deeper shade than ripe ones With basic dyestuffs on a tannin antimony mordant, unripe hairs are dyed only in the interior, while in ripe ones the colour is distributed evenly throughout With alizarin, para-red, and indigo, neps show up as light coloured streaks or patches Haller (*J S C I*, 1908, p 976) found that when treated with Schweitzer solution unripe hairs swell up but do not dissolve They develop a blue colour when treated with zinc-chlor-iodide solution much more quickly than ripe hairs A solution of iodine in potassium iodide colours ripe hairs a dark yellowish brown, whilst unripe hairs acquire only a light yellow colour If unripe hairs be immersed in a cold solution of sodium hydroxide they retain what twist they possess becoming only more transparent

Herzog (*J S C I* 1915, p 487) notes that while the term dead is applied to all thin-walled hairs which cause neps or light coloured spots in dyed fabrics, little attempt is made to differentiate between unripe and dead hairs All cotton contains the former, but the latter are derived chiefly from degenerated plants or those which have run wild These dead hairs are doubly refractive, showing colours under the polarising microscope, the insertion of a mica plate of 1 8 λ affording a ready means of detecting them Ripe hairs remain bright in all positions, but the broad, flat, dead hairs show black and white portions according to their relative positions in the field Unripe hairs show similar but less marked effects

The author recognises three types Type 1, the most common, is very irregular in breadth and structure, the walls are fairly thick but less so than those of the textile fibre The interior and even the walls are highly charged with coloured protein matters, beard fibres from Egyptian seeds showing 1 86 to 2 46 per cent of nitrogen against 0 49 to 0 54 per cent for the textile fibres, the lumen is often filled with protoplasm The cuticle is not strongly developed, but the fibres are charged with an excess of fatty matters in a similar degree to the protein They swell rather slowly in cuprammonium and the cell wall is thereby stratified into a large number of well differentiated layers, while the protoplasm remains insoluble Type 2 is exceptional, very rarely met with, the fibres are flat, ribbon like, very broad, often folded or twisted They are gradually dissolved by cuprammonium, without stratification The protoplasmic contents are deep brown in colour and present in very large quantities (*e g* 23 1 per cent of protein), especially near the base Type 3 occurs particularly in wild or degenerated plants, the fibres are similar in breadth to the textile fibres, with spiral structural markings at an angle of 50° to 63° C They are poor in protein, only lightly coloured, with cuticle only slightly developed, they dissolve in cuprammonium without special characteristics The interior of the fibres is often penetrated by fungus mycelium, which is stained by aniline blue-glycerin

Lack of lustre on mercerisation may generally be traced to the presence of incompletely ripened or otherwise abnormal fibres In order to test the mercer-

ising capacity, sections of the raw yarn, about 0·5 mm. long (*e g* ten separate sections), are mounted in a mixture of potassium hydroxide and glycerin on slides ruled with fine lines to facilitate counting. In each mount a hundred fragments are counted without selection, those which fail to show a perfectly cylindrical form being reckoned as non mercerised The proportion of cylindrical fragments is in direct relation to the lustre obtainable *e g* very high lustre, 93 to 98 per cent , satisfactory, 83 to 87 per cent.; inferior, 68 to 75 per cent.

An important paper by Clegg and Harland may be found in the *Journal of the Textile Institute*, 1923, T 125. Dealing with motes which resist the dyestuff they give the following conclusions —

1. The presence of motes and streaks of a lighter shade than the dyed background is mostly due to the presence of neps.



Fig 31.—Nep



Fig. 32 —Thin-walled hairs.

2 The neps consist of a matted tangle of thin-walled hairs which, in surface view, exhibit a glazed appearance

3. The thin-walled hairs are essentially of the type described originally by Crum as "dead" cotton.

4 Herzog's view that the difference in shade is purely an optical effect is substantiated on two main grounds (*a*) elimination of dispersion effects, by immersion in various mounting media, renders the difference in shade in dyed hairs practically negligible, and (*b*) in experimentally dyed cloth, the motes and streaks only appeared when the glazed surface of the neps was produced with a hot iron

A nep showing a tangle of thin-walled hairs is illustrated in fig. 31,[1] taken

[1] Illustration by courtesy of the British Cotton Industry Research Association

from Clegg and Harland's paper, while fig 32 [1] shows thin-walled hairs occurring in a parallel bunch in a dyed fabric, lighter in shade but not in the form of a nep.

Abnormal Hairs.—In addition to immature and dead hairs, certain other abnormal types are met with These have been described by Denham, *J. Text. Inst*, 1923, T 100 They include—

Branched hairs, of which an illustration is given in fig 33 [1]



Fig 33.—Branched hairs

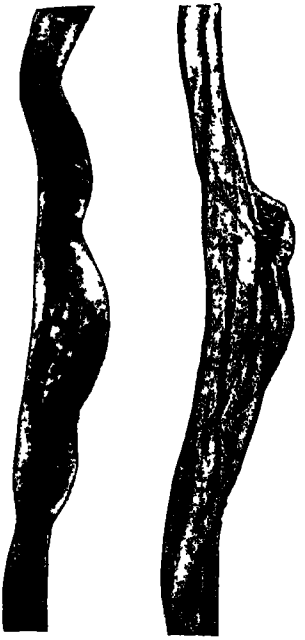


Fig 34.—Bulges.

"This branching occurs generally within a short distance of the tip of the hair, and is a response to reduced pressure on one side of the apex, caused by incomplete filling of available boll space, when longitudinal growth in one direction is arrested"

Bulges.—These consist of local enlargements of the hair, occurring often in conjunction with a bend They are fairly common in the coarser types of cotton. The hair may, for a short distance, assume a diameter several times the normal. Such fibres, naturally, cause trouble in spinning Examples are seen in fig 34

[1] Illustration by courtesy of the British Cotton Industry Research Association

CHAPTER VI.

THE CONSTITUENTS OF COTTON; PROTEINS AND AMINO COMPOUNDS; COLLOIDS; THE DETERMINATION OF PROTEINS.

THE natural constituents of raw cotton, as explained in the last chapter, are simply those of dried-up vegetable cells These include—

1. Cellulose, which in the case of the cotton hair constitutes nearly 90 per cent. of the whole
2. Proteins and simpler amino compounds
3. Pectoses, pectins, and pectic acids
4. Organic acids, such as tannic acid, and their salts
5. Oil and wax.
6. Mineral matter
7. Colouring matters
8. Water.

There is no very clear evidence as to the proportions in which the various constituents are present, since they are very difficult to separate Matthews (*Textile Fibres*) gives the following analyses of raw cotton - -

	Surat	American	Egyptian
Cellulose	91 55	91 00	90 80
Oil and wax	0 40	0 35	0 42
Protoplasm and derivatives	0 53	0 53	0 68
Mineral matter .	0 22	0 12	0 25
Water .	7 50	8 00	7 85

These figures, though commonly quoted, do not differentiate sufficiently, and ignore the pectoses and pectins Knecht and Hall (*J Soc Dyers and Col*, 1918, p. 220) classify the constituents according to their successive solubility in different solvents They give the following table for yarn and raw cotton —

	Raw Cotton		Cotton Yarn	
	Egyptian	Texas	American	Egyptian
Benzol extract	0 47	0 55	0 407	0 444
Alcohol „ . .	0 68	0 90	0 533	0 744
Water „ .	0 46	0 61	0 656	0 509
Ammonia „	0 45	0 39	0 425	0 500
Formic acid extract	0 46	0 72	0 650	0 405
Hydrochloric acid extract .		.	0 656	0 540
Total .	3 52	4 17	4 327	4 142

The benzol extract contains the oil and waxes Alcohol extracts an amorphous hygroscopic brown substance which contains 1 07 per cent of nitrogen and has a strong reducing action on Fehling solution Water removes some of the salts, soluble nitrogen compounds, and an amorphous brown colouring matter. Ammonia dissolves proteins and pectins while acids remove chiefly mineral matter Pectose is still unaccounted for, since it only gives soluble derivatives (pectates) on prolonged boiling with water or alkali

The following results obtained by the authors from brown Egyptian cotton may be quoted also —

Water	9 05
Mineral matter	0 99
Oil and wax	0 36
Matter soluble in alcohol	0 94
Proteins calculated from total nitrogen	3 99
Total matter soluble in boiling alkali	4 23

Cotton goods, as received by the bleacher, may contain, in addition to the natural impurities, such adventitious matters as lubricating oil, size, and dirt

The Nitrogenous Constituents of Cotton.

At least three kinds of nitrogen compounds are present in the cotton hair These are—

1 Proteins
2 Amino acids and amides
3 Complex nitrogenous compounds probably associated with the natural colouring matters which cannot, like proteins and amino acids, be removed by means of sodium hydroxide

The Proteins.—The proteins are complex organic compounds associated with animal and vegetable living matter They form the chief constituent of muscle, blood, nerves, and glands of all animals Protoplasm is itself composed largely of proteins No protein has been prepared synthetically in the laboratory, but it is thought that they are built up by protoplasm by the condensation of various amino acids

The proteins are, as a rule, colourless, solid substances They are generally amorphous though some are crystalline White of egg (egg albumin) dried at a low temperature is a typical protein

The proteins contain the elements carbon, hydrogen, oxygen, nitrogen, sulphur, and sometimes phosphorus The proportions vary somewhat with the origin of the substance The limits of variation in composition are given in the following table –

Carbon	50 55	per cent
Nitrogen	15 19	,,
Hydrogen	6 9 7 3	,,
Oxygen	19 24	,,
Sulphur	0 3–2 4	,,

The molecular weight of the proteins is not known with certainty, but it must be very high Egg albumin may have a molecular weight of about 14,000, while in the case of hæmoglobin it cannot be less than 16,000 This protein contains iron, and if only one atom were present in the molecule, the simplest formula consistent with its percentage composition would be $C_{758}H_{1203}O_{195}N_{21}FeS_3$ Casein, which combines with sodium hydroxide in definite proportions, is thought

to have a molecular weight of from 4540 to 6810, but, as a general rule, very few proteins can have a molecular weight of less than 10,000 The proteins vary in solubility Some are soluble in water, others sparingly soluble in water are more readily dissolved by dilute solutions of salt, while some are insoluble in both water and saline solutions but soluble in acids or alkalis All proteins are insoluble in alcohol and other organic solvents They can be precipitated from their solutions completely by the addition of alcohol They are thrown down also, in every case, when the solution is saturated with ammonium sulphate. Some are precipitated when their solutions are only half saturated with ammonium sulphate Others can be precipitated by means of magnesium sulphate, zinc sulphate or sodium chloride This method of precipitation is termed "salting out" Differences in the readiness with which proteins may be salted out are used, sometimes, as a basis for their classification, and are also of great use in their separation and purification

Solutions of proteins and particularly dilute alkaline solutions, are generally coagulated by acids, either at ordinary temperatures or at the boiling point, and many are coagulated by heat alone

These properties are made use of in the separation of proteins from animal or vegetable tissues and in effecting their purification The tissue is extracted with water, dilute alkali, or acid, or with a dilute solution of sodium chloride, and the solution thus obtained is precipitated by means of one of the salts mentioned, or by boiling, acidification, or the addition of alcohol The precipitate thus obtained is redissolved in water, dilute alkali or acid and reprecipitated. Separation from saline impurities may be effected also by dialysis (*vid* p 45)

There are many different proteins They may be divided into certain groups The system of classification generally adopted is based upon (1) a study of the products of their hydrolysis, and (2) the readiness with which they are precipitated from their solutions by ammonium sulphate, magnesium sulphate, or zinc sulphate Some of the proteins yield, as first products of hydrolysis, two substances, one of which is a typical protein and the other a non-protein Thus oxyhæmoglobin gives globin (protein) and hæmatin (non protein) Other proteins, like casein, contain notable quantities of phosphorus Based upon such considerations as these, the following scheme of classification is given by Cohen, *Organic Chemistry*, vol iii p 157 —

1 Protamines
2. Histones
3 Albumins and globulins
4 Glutelins and gliadins
5 Conjugated proteins (nucleoproteins, chromoproteins, glucoproteins)
6 Phosphoproteins
7 Unclassified proteins (scleroproteins)
8 Protein derivatives (metaproteins, proteoses, peptones, polypeptides)

The more important classes (Perkin and Kipping, *Organic Chemistry*, vol ii p 577) are—

(*a*) The **albumins** (egg albumin and blood albumin), which are soluble in water and are not precipitated when their solutions are saturated with sodium chloride or magnesium sulphate

(*b*) The **globulins** (serum globulin), which are insoluble in water but soluble in dilute salt solutions, from which they are precipitated when their solutions are saturated with magnesium sulphate

(c) The **phosphoproteins** (casein), which contain phosphorus and have an acidic character. They dissolve in alkalis, giving solutions which do not coagulate when heated.

General Reactions of Proteins.

1 Solid proteins, when heated alone, or with soda lime, give off ammonia, and, in some cases, also sulphuretted hydrogen When proteins such as keratin, which contain a large proportion of sulphur, are dissolved in boiling sodium hydroxide and lead acetate is added to the solution, a black precipitate of lead sulphide is produced

2 Aqueous solutions of proteins are optically active, being strongly lævo-rotatory

3 Neutral or faintly acid solutions of most proteins are coagulated when heated to 100° C Small quantities of free alkali, or excess of acid, prevent the coagulation Proteins are generally precipitated also, when their neutral or alkaline solutions are poured carefully on to the surface of nitric acid The test may be rendered more delicate in the following manner. One volume of nitric acid (sp. gr 1 42) is mixed with five volumes of a saturated cold aqueous solution of magnesium sulphate Some of this mixture is placed in a test-tube, and the solution of the protein is poured carefully down the side of the test-tube, so that the two liquids do not become mixed The formation of a turbidity at the junction of the two liquids indicates the presence of a protein

4 Picric acid precipitates proteins from solutions made faintly acid with acetic acid Phenol and tannic acid act in a similar manner Almen's tannic acid reagent may be used It is made by dissolving 4 grammes of tannic acid in 190 c c of 50 per cent spirit and adding 8 c c of 25 per cent acetic acid. Phosphotungstic and phosphomolybdic acids also precipitate all proteins

5 Potassium ferrocyanide, when added to a solution of a protein made faintly acid with acetic acid, produces a flocculent white precipitate

6. **Colour Reactions.**—All proteins give certain colour reactions which are very useful for their detection. The chief of these are—

(*a*) The xanthoproteic reaction. When concentrated nitric acid is added to a solid protein a deep yellow colour is produced due to the formation of xanthoproteic acid The colour is changed to orange by alkalis A solution of a protein gives the same reaction when warmed with nitric acid.

(*b*) A solution of a protein when treated with Millon's reagent gives a white precipitate which becomes red on warming The production of this colour is due to the presence of tyrosine groups Millon's reagent is made by treating metallic mercury with an equal weight of nitric acid (sp gr 1·4), and, after the reaction has ceased, cooling the mixture and diluting it with twice its volume of water. It consists of a solution of mercurous nitrate containing nitrous acid.

(*c*) Solid proteins are dissolved when heated with hydrochloric acid with the production of a violet solution.

(*d*) The Biuret reaction is given by all proteins To a solution containing protein a little copper-sulphate solution is added, followed by an excess of sodium-hydroxide solution. When the precipitate has settled down, the supernatant liquor has a violet or violet-blue colour.

The Action of Heat on Solutions of Proteins.—It has been mentioned above that, in many cases, aqueous solutions of proteins are coagulated by heat. The temperature at which coagulation takes place varies with the protein, but as a general rule it is between 55° C. and 75° C.

Colloidal Properties of Proteins.—Proteins are typical colloids, that is, when dissolved in water they are unable to pass through a parchment membrane. Their solutions exhibit also all the other important properties of colloidal solutions. It was discovered by Graham, in 1861, that most substances, when dissolved in water, are able to pass or "diffuse" through a paper parchment membrane, but that some are unable to, or only do so very slowly. Salts, sugar, peptone, and many other bodies belong to the former class. Since it contains all the soluble crystalline salts, these bodies were termed by Graham "crystalloids" Substances which, like glue, are unable to pass through the membrane were called "colloids," from *kolla* which is the Greek word for glue. Other important colloids are the starches, gums, proteins, and soaps, all of which are of importance in cotton bleaching In studying the phenomenon of diffusion an apparatus termed a dialyser is made use of. This may conveniently consist of a seamless tube made of paper parchment which is suspended in a flask containing water (fig 35). The tube must be tested before use to see that it does not leak. It is then filled with the solution to be examined and placed in a conical flask filled with distilled water The flask should be made of a hard, insoluble glass, and only freshly distilled water condensed by means of a hard glass condenser should be used For details of other types of apparatus, Hatschek's *Physics and Chemistry of Colloids* may be consulted

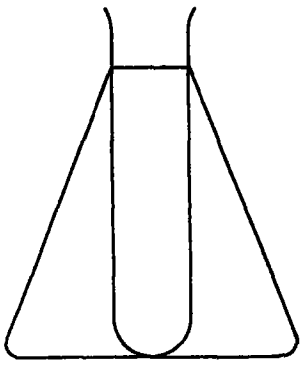


Fig 35.—Dialyser

If a solution of a colloidal substance, such as glue, to which some salt has been added, be placed in the dialyser, the salt will pass through the membrane into the water, until a state of equilibrium has been reached, when as much passes in one direction as the other If, however, the flask be now filled with fresh distilled water, diffusion again sets in, and by changing the water frequently the whole of the salt may be removed and thus separated from the colloidal glue Different diffusible bodies pass through the membrane at different rates Thus, hydrochloric acid diffuses more quickly than sodium chloride, which, in turn, has a greater rate of diffusion than sugar. Even colloids diffuse to a small extent

Chemical compounds cannot be divided, definitely, into two classes, "crystalloids" and "colloids" Many are capable of existing in both forms. Thus, colloidal solutions of gold, silver, sodium, and other metals can be obtained, and, also, of many other bodies such as ferric hydroxide Hence the term "colloid" is regarded as a state in which matter can exist and not as a particular kind of matter.

A colloidal solution of ferric hydroxide may be prepared very easily in the following manner About 500 c c. of water are heated to the boiling-point in a beaker or flask While boiling, 5 c c of a 33 per cent. solution of ferric chloride are added The colour of the solution changes to brownish red and a stable solution of ferric hydroxide is produced, containing also hydrochloric acid liberated by hydrolysis

$$Fe_2Cl_6+6H_2O=Fe_2(OH)_6+6HCl.$$

The hydrochloric acid may be removed, if desired, by dialysis If ammonia be added to the solution, the ferric hydroxide is precipitated Ordinary ferric hydroxide prepared by precipitation does not dissolve in water.

The Properties of Colloidal Solutions.—The properties of colloidal solutions differ from those of ordinary solutions of crystalline salts in many respects. In the first place, they are generally slightly opalescent in appearance. This is seen well in solutions of egg albumin or starch.

When a crystalline salt is dissolved in water, only a definite quantity can be taken up by any given volume of water When the saturation point is reached, no more can be dissolved With colloidal solutions there is no definite point corresponding to this Thus, glue will dissolve in water in practically all proportions.

Colloidal solutions are capable of existing in two forms. While a hot solution of gelatin in water is perfectly liquid, when allowed to cool it sets to a jelly the firmness of which depends upon the amount of gelatin present If the colloidal solution of ferric hydroxide described above be kept for a long time, a gelatinous precipitate is produced When a solution of white of egg in water is heated, the albumin either becomes coagulated, or the solution sets to a white gelatinous mass. A hot solution of starch when allowed to cool forms a thick paste or jelly Sometimes, as in the case of gelatin, the solid passes again into the liquid form on heating, but colloids, such as albumin, when once coagulated become insoluble in water. Some colloidal substances, like gum arabic, neither set on cooling nor become coagulated when heated The two states in which a colloid can exist are distinguished by the terms "hydrosol" (or sol) and "hydrogel" (or gel) *The hot fluid solution of gelatin in water is called a "sol," or the gelatin is said* to be in the sol condition The jelly, produced when the solution is cooled, is called a "gel," or the colloid is said to be in the gel condition In the case of egg albumin the cold solution is the sol, the gel being formed on heating With ferric hydroxide, the gel is formed simply on standing or when a small quantity of an electrolyte is added Thus, if a small quantity of sodium sulphate be added to a hot ferric hydroxide sol, coagulation takes place at once, the whole of the ferric hydroxide forming a flocculent precipitate (or gel)

It may be mentioned that, when speaking of colloidal solutions, it is usual to term the dissolved colloid the "disperse" and the solvent the "continuous" phase respectively

The large molecular weight of protein has been mentioned It is probable that colloids owe their inability to pass through a dialysing membrane either to the size of their molecules, or to these molecules forming molecular complexes or aggregates which are larger than the pores of the membrane.

Bechold prepared membranes, which he terms "ultra-filters," in which the actual size of the pores can be measured One method of preparing these ultra-filters consists of impregnating hard filter-paper with a solution of collodion and then washing away the solvent by immersing the treated paper in water The size of the pores depends upon the concentration of the nitrocellulose solution used, varying between 930 to 21 millionths of a millimetre By means of these filters, it is possible to obtain some idea of the size of the molecules or aggregates which will not pass through Similar evidence is obtained by means of the ultra-microscope (*vide* Hatschek, p 15), which enables the size of the actual particles present in a colloidal solution to be measured, if they exceed 5 millionths of a millimetre in diameter When colloidal solutions are examined by these methods, it appears that, in most cases, the colloid is present in particles which are much larger than those which would correspond with any molecular weight determined by purely chemical or physical methods of investigation.

In fact, it seems that the substance is really suspended in the liquid, in a very finely divided state, each particle consisting of a cluster of molecules of the

colloid, these clusters being too large to pass through the pores of the dialysing membrane In a solution of a crystalloid, such as sodium chloride, the molecules are present as such Thus the difference between the two solutions may be simply one of molecular complexity

Colloidal solutions have, as a rule, a high viscosity, that is, flow comparatively slowly through a capillary tube or fine orifice They owe many of their applications, such as the manufacture of artificial silk, to this property When a salt is dissolved in water the solution does not show any marked increase in viscosity Colloidal solutions fall into two classes with regard to the increase in viscosity compared with water or any other solvent In the first class are those, such as colloidal solutions of the metals, whose colloidal solutions have only a slightly increased viscosity The second class contains chiefly organic colloids such as gelatin or starch In these cases, very small quantities of the colloid produce a marked increase in the viscosity of the solution It is believed that in those solutions which have a low viscosity the disperse phase is present as solid particles, while in the sols with a high viscosity the disperse phase is liquid An albumin sol, for example, would consist of a dilute solution of albumin in which are dispersed drops or globules consisting of a much more concentrated solution When a liquid contains solid particles of microscopic size, the term " suspension " is employed, while when there are two liquid phases, we have what is known as an ' emulsion ' The sols are called ' suspensoids " and " emulsoids " respectively The suspensoids are less stable than the emulsoids Their coagulation is generally brought about readily by small quantities of electrolytes If, however, a small quantity of an emulsoid be added, the suspensoids become much more stable requiring a comparatively large amount of an electrolyte to cause their coagulation Emulsoids used for this purpose are termed " protective colloids " This phenomenon is observed, often, in the course of ordinary chemical analysis It is found, for example, that many inorganic precipitates are difficult to obtain in a solution containing even a little gelatin, a colloidal solution being produced which in some cases passes through a filter paper

The term protective colloid is used also in rather a different sense in textile chemistry For example, the presence of glue is said to protect wool from damage by caustic alkalis This is due probably to another very important property of colloids, namely their power of forming '*adsorption* compounds "

Adsorption is not confined to colloids Charcoal owes many of its applications to its power of ' absorbing gases and colouring matters When an aqueous solution of acetic acid is shaken with powdered charcoal and filtered, the filtrate contains less acetic acid than the original solution Some of it has been retained by the charcoal

In dilute solutions the disappearance of the acid is nearly complete, but in more concentrated solutions the concentration of the acid in the charcoal increases less rapidly with increasing concentration of the aqueous solution The removal of the acid is not due to chemical action for the following reasons —

1 Charcoal acts in the same way towards inert gases such as nitrogen

2 If definite chemical combination occurred, the concentration of the acid in the water would remain constant till all the charcoal had been converted into the new compound, then the concentration of the acid in the water would rise rapidly But, actually, there is a continuous steady increase of the concentration of the acid in the water

Many other bodies are adsorbed from their solutions by charcoal Two examples may be given (1) If an aqueous solution of quinine sulphate be shaken with finely powdered charcoal and filtered the filtrate no longer tastes bitter.

(2) When a dilute solution of treacle is treated in the same way a colourless filtrate is obtained

Cotton cellulose acts in the same manner When it is soaked in a solution of sodium hydroxide and squeezed out, the concentration of the sodium-hydroxide solution will be found to be less than it was before Or, when cotton is soaked in a solution of copper sulphate it removes some of the salt from the solution In all of these cases adsorption compounds are said to be formed Not only may a soluble substance be taken out of its solution, but a solid undissolved body may become changed into a colloidal adsorption compound and taken into solution Thus a solution of soap in water will remove particles of dirt, or iron oxide, from a cotton fabric and produce an emulsion which is capable of carrying the particles through an ordinary filter paper

Slater (*J S C I*, 1925, p 161) gives the following description of adsorption "Substances in contact try to mix and do so in many cases Lead and zinc, pressed together, form eventually a homogeneous solution Alcohol poured into water forms a solution, but the mixing has to begin at the surfaces where the two liquids first meet When the molecules of the two bodies intermingle completely to form a homogeneous solution or mixture, the process is termed *absorption* The tendency to intermingle is always present, but intermingling is often prevented by resistance to diffusion The substances can then only concentrate at the boundary surface, in the attempt to mix with one another This concentration of one substance at the surface separating it from another, providing a layer of increased concentration, only a few molecules thick at most, is called *adsorption* The molecules constituting all substances are in a state of incessant motion When a molecule strikes against a solid or liquid surface, one of two things happen (1) the molecule may be reflected, *i e* it may bounce off again, or (2) it may condense on the surface, *i e* it may be held by attractive forces in such a way that it forms, at least temporarily, a part of the solid body If any molecules are held to the surface in this way, even for a short time only, a certain time interval must elapse before they can evaporate This time lag will bring about an accumulation of molecules on the surface, and may thus be looked upon as the cause of adsorption Neglecting the special attractive forces which cause this time lag, the considerations affecting adsorption are –

'1 The number of molecules striking the surface

'2 Their speed

The former depends on the pressure in the case of a gas or upon the concentration in the case of a liquid while the speed depends upon the temperature"

The effect of pressure or concentration is seen in the case of charcoal, which adsorbs gases under pressure much more readily than at atmospheric conditions In the case of liquids, such as a solution of acetic acid, Schmidt found that when animal charcoal was treated with a solution of acetic acid in water the amount of acid retained by the charcoal increased with the concentration of the solution, in the manner shown in the following table, when 5 grammes of charcoal and 100 c c of acetic acid were used –

Acid adsorbed by charcoal	0 93	1 15	1 248	1 43	1 62
Acid remaining in water	0 036	0 084	0 13	0 206	0 350
$\frac{C_c^4}{C_w}$	205	208	180	203	197

C_c—concentration of acid in charcoal

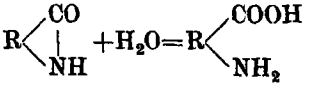
C_w – „ „ „ water

It is seen, from this table, that (*a*) the adsorption is nearly complete in dilute solutions but not so complete in more concentrated solutions, (*b*) the concentration of the acid in the charcoal increases less rapidly with increasing concentration of the acid in water The adsorption goes on till a state of equilibrium is reached, depending upon the concentration and temperature (or pressure in the case of a gas) Alteration in either of these conditions destroys the equilibrium, and this either increases or decreases the amount of acid adsorbed. The process is, in fact, *reversible*. But in the case of acetic acid and water, Schmidt found that $\frac{C_c^4}{C_w}$ was a constant. The relation between the quantity adsorbed and the concentration of the solution is given by the formula of Freundlich, viz. $V=KC^{\frac{1}{n}}$, where V=the amount adsorbed, C=the concentration of the liquid, K and *n* being constants depending on the nature of the solution and adsorbent. This equation expresses the fact, established above, that adsorption increases as the pressure or concentration increases, though more slowly Adsorption is exhibited chiefly by bodies which have a large surface, like colloidal molecular aggregates or porous substances such as charcoal Gibbs showed that it is connected with the surface tension between the solid and liquid, a substance being adsorbed to a large extent only when it lowers the surface tension between the solid and the liquid, and when the surface tension is increased there is very little adsorption. "If a dissolved substance has the property of lowering the surface tension of the solution at any particular face, then the solute will exist in a higher concentration at that face than in the general bulk of the solution" This is the first step in adsorption, and this concentration may cause super-saturation at the face, and consequent deposition of the solute, or a solid solution or some chemical compound may be formed as a result of this. Although adsorption is essentially a reversible action, the adsorbed substance may become changed and removed from the sphere of action, thus making the process irreversible In dyeing, for example adsorption is followed by the formation of an insoluble compound of the dyestuff with the fibre, thus preventing the establishing of an equilibrium Hence adsorption and fixation proceeds till the dye-bath is exhausted.

Amphoteric Nature of Proteins.—Proteins have both acid and basic properties. This is denoted by the term "amphoteric" Some proteins have the acid more marked than the basic properties, while, in others, the reverse is the case In casein the acid properties are strongly developed, while the protamines are highly basic When a little acetic or hydrochloric acid is added to a solution of egg albumin, acid albumin is formed. The solution is no longer coagulated when heated to 70° C, but, after exact neutralisation, a flocculent white precipitate is obtained which is readily soluble in dilute alkalis When treated in a similar manner with very dilute alkali, egg albumin gives alkali albumin Its solution is coagulated by boiling, and gives a precipitate when neutralised with acid. These acid and basic properties are probably connected with the presence of amino and carboxyl groups These may be in the form of an internal anhydride



which is hydrolysed by water, thus.



But it is interesting to note that when a protein is deaminated, it still has basic properties This has led to the opinion that the amphoteric properties may be connected with —CONH— groupings. It may be mentioned that deamination consists of replacing amino by hydroxyl groups by first forming the diazo compound and boiling this with water or dilute acid, thus .

$$R\,NH_2 + HONO + HCl = R-N:N-Cl + 2H_2O,$$
$$R-N:N-Cl + H_2O = R\,OH + N_2 + HCl.$$

The Chloramine Reaction.—When a solution of a protein, proteose, or peptone is treated with chlorine, a compound termed a chloramine is formed, with the liberation of hydrochloric acid Similar compounds are produced with bromine, iodine, or a soluble hypochlorite A chloramine is an amine in which an atom of hydrogen has been replaced by chlorine The simplest, NH_2Cl, is obtained when chlorine acts on a solution of ammonia—

$$NH_3 + Cl_2 = NH_2Cl + HCl.$$

Organic chloramines, of the type R NHCl, are formed in accordance with the equations

$$RNH_2 + Cl_2 = RNHCl + HCl,$$
$$RNH_2 + NaOCl = RNHCl + NaOH.$$

These chloramines may be either soluble, sparingly soluble, or insoluble in water In the case of gelatin, Rideal and Stewart (*Analyst*, 1897, p. 228) found that the whole of the protein was completely precipitated when its aqueous solution was saturated with chlorine gas. Allen and Searle (*Analyst*, 1887, p 258) obtained similar compounds with bromine, while Hopkins and Brooks (*J. Physiol*, pp 22, 184) found that iodine reacted in the same manner The importance of chloramines in cotton bleaching was first recognised by Cross, Bevan, and Briggs (*J S C I*, 1908, p 261), who observed that, if the nitrogenous constituents of cotton or flax are not removed completely before bleaching, soluble chloramines tend to accumulate in the bleach liquors, and to become fixed on the fabrics These insoluble, or fixed, chloramines are not removed by the subsequent scouring or washing When cotton containing chloramines is stored, these bodies decompose gradually with the formation of hydrochloric acid as one product This hydrochloric acid causes the cotton to become tendered Chloramines liberate iodine from an acidified solution of potassium iodide and, when treated with sulphurous acid, exchange their chlorine for hydrogen, the original amino compound being formed—

$$RNHCl + 2HI = RNH_2 + HCl + I_2,$$
$$2RNHCl + 2H_2SO_3 + 2H_2O = 2RNH_2 + 2HCl + 2H_2SO_4.$$

The second of these reactions is of importance in the chlorination of wool. In this process, the fabrics are treated with an acidified solution of bleaching powder Chlorine is adsorbed and chloramines are also formed The goods are then soaked in a bath of sodium bisulphite, to remove both the adsorbed and combined chlorine. Chloramines are not decomposed by hydrogen peroxide. Cross, Bevan, and Briggs (*loc cit*) distinguish between adsorbed and combined chlorine in the following manner If cotton contain either chloramines, chlorine, or hypochlorite, it liberates iodine from an acidified solution of potassium iodide. If, however, it be washed with acidified hydrogen peroxide, the chlorine and hypochlorites are decomposed, leaving the chloramines—

$$Cl_2 + H_2O_2 = 2HCl + O_2$$

After washing with water, the last traces of hydrogen peroxide are removed by carefully adding an acidified solution of potassium permanganate, till a faint pink colour is produced. The cotton is again washed. If it still liberates iodine from potassium iodide, chloramines are present.

Briggs (*J S.C.I*, 1918, p. 447 R) makes use of the chloramine reaction as a qualitative test for deposits of protein. Stains of protein fluids on fabrics, the presence of wool fibres in cotton, or of glue or casein in adhesives, are easily demonstrated by chlorinating, washing, and developing the colour with potassium iodide and starch

The Hydrolysis of Proteins.—When proteins are hydrolysed, they are first changed into soluble compounds These in turn are hydrolysed into simpler, though still complex, bodies which, upon prolonged hydrolysis, yield a mixture of simple amino acids These stages of hydrolysis are represented thus.

Proteins → proteoses → peptones → polypeptides → amino acids.

This hydrolysis may be brought about by the action of either (1) acids, (2) alkalis, (3) enzymes, but the course of the reaction is the same in all cases

The proteoses have a lower molecular weight than the proteins from which they are formed They are no longer coagulable by heat, although they are precipitated by saturating their solutions with ammonium sulphate They are precipitated with nitric acid in the cold, and give a reddish-violet biuret reaction They are slightly diffusible.

The peptones have lower molecular weights than proteoses They are readily diffusible and non-coagulable They are not precipitated by nitric acid, and give a pink colour with the biuret reaction.

The polypeptides are still simpler in composition than the peptones, and may be regarded as simple peptones They are of great importance, because they can be built up by the condensation of amino acids Thus, if two molecules of aminoacetic acid (glycine) unite with the elimination of water a dipeptide is obtained Thus

$$COOH\ CH_2NH_2 + HOOC\ CH_2NH_2 = H_2O + COOH\ CH_2NH.CO\ CH_2NH_2$$

This dipeptide can be condensed with another molecule of the amino acid, giving a tripeptide—

$$COOHCH_2NH\ CO\ CH_2NH_2 + HOOC\ CH_2NH_2 = H_2O + COOH\ CH_2NH\ CO\ CH_2NH\ CO\ CH_2NH_2$$

And if the process be continued after many such repetitions a polypeptide is obtained Emil Fischer synthesised an octadecapeptide with a molecular weight of 1213, which has many properties in common with peptones Thus it gives the biuret reaction, is precipitated from its solutions by mixtures of the original amino acids The polypeptides with long chains, containing different amino acid radicles, show the greatest resemblance to peptones It is believed that proteins are built up from amino acids in a manner similar to that just described for polypeptides, *i e* by condensation with elimination of water (*vide* also p 52)

Amino Acids and Amides.—An amino acid is an organic acid in which one or more hydrogen atoms of the radicle are replaced by the amino (NH_2) group. The simplest amino acid is carbamic acid or amino formic acid, NH_2COOH, but it is not known in the free state. Its homologue, aminoacetic acid or glycine,

CH_2NH_2COOH, is obtained as an ammonium salt, when chloracetic acid, $CH_2ClCOOH$ is dissolved in a strong aqueous solution of ammonia Thus

(1) $CH_2ClCOOH+NH_4OH = CH_2NH_2COOH+HCl+H_2O$
(2) $CH_2NH_2COOH+NH_4OH = CH_2NH_2COONH_4 + H_2O$
(3) $HCl + NH_4OH = NH_4Cl + H_2O$

Glycine is a colourless crystalline substance, which has a sweet taste and dissolves readily in water Since it contains an amino group, it has basic properties, while, owing to the presence of the carboxyl group, it is also an acid The substance itself has a neutral reaction to litmus When treated with bases the corresponding salts are obtained Thus, when the ammonium salt is boiled with cupric hydroxide the copper salt is produced which crystallises out as blue needles when the solution is cooled

$$2CH_2NH_2COONH_4+Cu(OH)_2=(CH_2NH_2COO)_2Cu+2NH_3+2H_2O$$

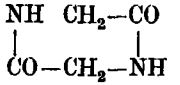
In this reaction, glycine plays the part of an acid But if glycine be dissolved in hydrochloric acid and the solution crystallised, glycine hydrochloride, $CH_2NH_2HCl\ COOH$ is obtained in which the amino acid acts as a base When glycine is treated with nitrous acid, the amino group is replaced by a hydroxyl group (forming hydroxy acetic acid) and nitrogen is liberated

$$CH_2NH_2COOH+HONO=CH_2OH\ COOH+N_2 + H_2O$$

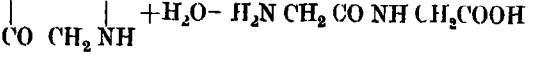
Amino acids give rise to esters, like other carboxylic acids When for example, glycine is dissolved in alcohol and the solution saturated with dry hydrochloric acid gas, the ethyl ester is obtained as a hydrochloride –

$$CH_2NH_2COOH + C_2H_5OH = CH_2NH_2COOC_2H_5 + H_2O,$$
$$CH_2NH_2COOC_2H_5 + HCl = CH_2NH_2HCl\ COOC_2H_5$$

These esters are of much importance in the synthesis of polypeptides Glycine ethyl ester, in the presence of water, becomes changed into glycine anhydride, or diketo piperazine—



When this body is hydrolysed with hot concentrated hydrochloric acid, a hydrochloride of glycylglycine is produced–



This compound is a dipeptide When it is treated with chloracetyl chloride $CH_2Cl\ COCl$, the following reaction takes place

$$COOH\ CH_2\ NH\ CO\ CH_2NH_2 + ClCH_2COCl = COOHCH_2NHCO\ CH_2\ NH\ COCH_2Cl+HCl$$

This body, in turn, when treated with ammonia yields a tripeptide, $COOH\ CH_2NH\ CO\ CH_2NH\ CO\ CH_2NH_2$ If the process be repeated a tetrapeptide is obtained, another $COCH_2NH_2$ being substituted for one atom of amino hydrogen

Some amino acids contain closed rings, or aromatic radicles The most

important is tyrosine (or p-hydroxy-phenyl-α-aminopropionic acid), which has the formula

$$OH\langle\_\_\_\rangle CH_2\ CH\ NH_2\ COOH.$$

The amides are derived from carboxylic acids, by replacing the hydroxyl by an amino group, or from ammonia, by replacing a hydrogen atom by an acid radicle Thus, when acetyl chloride is treated with ammonia, the following reaction takes place —

$$CH_3COCl+NH_3=CH_3CONH_2+HCl,$$
$$NH_3+HCl=NH_4Cl$$

The compound CH_3CONH_2 is an amide known as acetamide It may be prepared also by the action of ammonia on ethylacetate

$$CH_3COOC_2H_5+NH_3=CH_3CONH_2+C_2H_5OH$$

Acetamide is a colourless crystalline body which melts at 82° C and boils at 222 C It is readily soluble in water or alcohol It has the odour of mice When heated with mineral acids, or with alkalis, it is decomposed, yielding acetic acid and ammonia

$$CH_3CONH_2+H_2O=CH_3COOH+NH_3$$

Asparagine, the amide of aspartic acid (aminosuccinic acid) has the formula $NH_2\ CO\ CH_2\ CH\ NH_2\ COOH$ It is found in the growing parts of many plants, and particularly in asparagus When heated with an alkali, it yields ammonia and aspartic acid, $COOH\ CH_2\ CH\ NH_2\ COOH$

Both amino acids and amides are found in plant tissues, for, not only are they required by the plant in order to build up protoplasm, but they are, also, the final products of the waste or breaking down of nitrogenous tissues That is, they play a part in both metabolism and katabolism

The amino acids produced by the hydrolysis of proteins include—

1 Monobasic monamino acids
2 Dibasic monamino acids
3 Diamino acids
4 Hydroxy and thio monamino acids
5 Heterocyclic amino acids
6 Aromatic amino acids

Among these monobasic monamino acids are

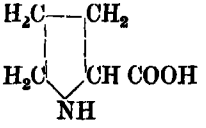
Glycine (aminoacetic acid) $(H_2N)CH_2COOH$
Alanine (α aminopropionic acid) $CH_3CH(NH_2)COOH$
Valine (α aminoisovaleric acid) $(CH_3)_2CH\ CHNH_2COOH$
Leucine (α aminoisobutylacetic acid), $(CH_3)_2CH\ CH_2\ CH(NH_2)COOH$
Isoleucine (secondary butyl), (α aminoacetic acid) $\begin{matrix}C_2H_5\\CH_3\end{matrix}\rangle CH\ CH(NH_2)COOH$
Caprine (α-aminocaproic acid) $CH_3(CH_2)_3CH(NH_2)COOH$

Aspartic acid (aminosuccinic acid) $CH\ NH_2COOH\ CH_2COOH$ and glutamic acid (aminoglutaric acid) $CH\ NH_2COOH\ CH_2\ CH_2COOH$, are dibasic monamino acids Wheat proteins give 30 per cent of glutamic acid when hydrolysed These bodies have well marked acid properties

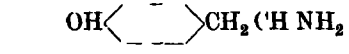
The diamino acids are strongly basic The most important are arginine and lysine The latter is derived from caproic acid, and has the formula $NH_2\ (CH_2)_4CH\ NH_2\ COOH$

Among the hydroxy- and thio-amino acids is serine, a product of the hydrolysis of silk proteins It is α-amino-β-hydroxy propionic acid, $CH_2(OH)CH\ NH_2COOH$

The heterocyclic amino acids are typified by proline (α pyrrolidine carboxylic) acid, which has the formula



Oxyproline is a mono-hydroxy derivative of proline The aromatic amino acids are represented by tyrosine and phenylalanine The latter is α-amino-β phenyl propionic acid, $C_6H_5\ CH_2\ CH\ NH_2COOH$, and tyrosine is its oxy derivative with the hydroxyl group in the para position, thus



It was mentioned, above, that the colour given by proteins with Millon's reagent depends upon the presence of a tyrosine group Different proteins when hydrolysed give mixtures of different amino acids This may be illustrated by one or two examples

	Egg Albumin	Gliadin (Wheat)	Keratin (Horn)	Gelatin
Glycine	0 0	0 02	0 34	25 5
Alanine	2 2	2 0	1 20	8 7
Valine	2 5	0 2	5 70	0 0
Leucine	10 7	5 61	13 80	7 1
Aspartic acid	2 0	0 58	2 50	3 4
Glutamic acid	9 1	37 33	3 00	5 8
Serine		0 13	0 68	0 4
Cystine		0 45	7 00	
Lysine	3 76	0 0		5 9
Arginine	4 91	3 16		8 2
Proline	3 56	7 06	3 60	9 5
Oxyproline				14 1
Histidine	1 71	0 61		0 9
Phenylalanine	5 07	2 35	3 00	1 4
Tyrosine	1 77	1 2	4 58	0 01

The separation of these amino acids is very difficult In the case of the mono amino acids it may be effected by converting them into their esters, by treatment with alcohol and hydrochloric acid The esters are liberated from the hydrochlorides formed by means of sodium hydroxide The solution is then saturated with potassium carbonate and the free esters extracted with ether These esters are then separated by fractional distillation, *in vacuo*, the fractions hydroysed and the liberated amino acid identified

The animal albumins are readily soluble in distilled water and are less readily salted out from their solutions than the globulins While, like all proteins, they are precipitated completely when their solutions are saturated with ammonium sulphate, they are not precipitated by either sodium chloride or magnesium sulphate When hydrolysed, they yield most of the amino acids,

and also a glucosamine, *i.e.* a derivative of glucose containing the group $-CH(NH_2)CHO$ The albumins are coagulated by heat and acids. They combine with formaldehyde, giving insoluble addition compounds.

The vegetable albumins resemble the animal albumins in most of their properties, but, as a rule, they are more readily salted out from their solutions

The globulins are insoluble in pure distilled water, but dissolve readily in water containing small quantities of inorganic salts They may be precipitated from these solutions by diluting with pure water. They dissolve readily in dilute alkaline solutions, from which they are precipitated by weak acids. They are more easily salted out from their solutions than the albumins, being thrown down by saturation with magnesium sulphate, or when their solutions are half saturated with ammonium sulphate They give most of the amino acids when hydrolysed and, also, a glucosamine. The proteins of cotton are chiefly albumins or globulins.

The conjugated proteins are of some importance The group contains very complex proteins, which can be broken down, by the action of acids or enzymes, into two portions One of these is a complex protein and the other a simpler non-protein Thus, hæmoglobin gives globin and hæmatein. Chlorophyll has a somewhat similar nature.

The Estimation of Proteins.

Proteins are almost invariably determined from their nitrogen content. Although this varies somewhat for different proteins, yet for most purposes the percentage of nitrogen multiplied by 6 33 gives the protein present with fair accuracy Nitrogen in organic compounds may be estimated in two ways viz (1) by Dumas' method, (2) by Kjeldahl's method. The latter is used in all industrial processes, but the former is sometimes employed where great accuracy is required. Since the determination of nitrogen is of great importance, these methods may be described here

Dumas' Method.—The following are the details of the method A piece

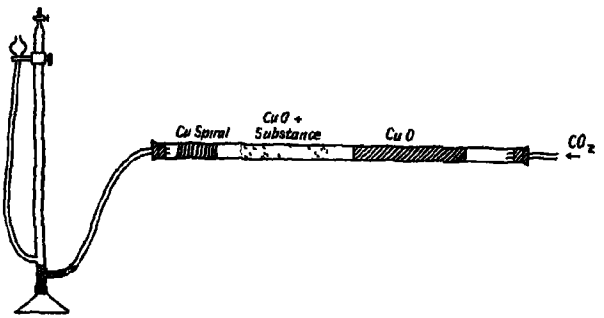


Fig 36.—Dumas apparatus

of combustion tube is thoroughly cleaned by means of strong sulphuric acid, washed and dried. *It is then fitted with corks and delivery tubes, one of which* leads to a Kipp apparatus for the delivery of carbonic acid, the other being connected with a nitrometer, as shown in fig. 36.

The tube is then plugged with asbestos at about 6 inches from the end at which the carbonic acid enters, and about 12 cm of powdered copper oxide

are introduced, the tube being held in nearly a vertical position About half a gramme of the substance is then mixed in a mortar with finely powdered copper oxide and the mixture introduced carefully into the combustion tube, the layer occupying the space of about 3 to 4 cm Copper oxide is now added until the tube is nearly full, when a roll of freshly reduced copper gauze is inserted The tube is then laid upon a bench and gently tapped in order to make a channel for the escape of the gases, after which it is placed in the furnace and connected with the carbonic acid generator and the nitrometer The front portion of the tube, namely that which does not contain the organic matter, is now heated until a dull red colour is produced The carbonic acid is then passed through the tube until the whole of the air has been expelled This will be indicated by the complete absorption of the bubbles as they rise in the nitrometer, which is filled with 50 per cent solution of caustic potash So long as any gas is collected in the nitrometer the apparatus will not be free from air When no further increase is noticed let the gas escape by opening the tap, readjust the levels, and collect again If, after a few minutes, no more gas is collected the apparatus will be free from air The portion of the tube containing the organic matter is now very gently heated, the stream of carbonic acid being continued The nitrogen which is produced will be carried through the apparatus with the excess of carbonic acid, the latter dissolving in the potash and leaving the nitrogen The combustion is continued until there is no further increase in the volume of the gas collected that is, until the bubbles are completely absorbed before they reach the surface In order to complete the absorption, a little fresh potash solution is now carefully introduced by means of the cup, after which the levels are carefully adjusted and the volume of nitrogen read off The atmospheric pressure and temperature are then taken, and the volume of the gas reduced to normal temperature and pressure by means of the following formula

Since the volume v is measured at t' under a pressure of $B-w$, where $w=$ tension of aqueous vapour in mm of mercury at a temperature $t°$, the volume v at 0° and 760 mm would be

$$v\times\frac{B-w}{760}\times\frac{273}{273+t'}$$

Example 0 2248 grm substance gave 7·1 c c Nitrogen at 16° B=753·5 mm., w=13 5 The weight of the gas, therefore, is

$$7\cdot1\times\frac{740}{760}\times\frac{273}{289}\times0\cdot001251=0\ 00818\text{ grm},$$

and the percentage of nitrogen,

$$\frac{0\ 00818\times100}{0\ 2248}=3\cdot63$$

1 c c of nitrogen at normal temperature and pressure weighs 1 254 mgm , hence the weight of nitrogen in mgm contained in the quantity of organic substance taken is found by multiplying the number of c.c of nitrogen obtained by 1·254.

Kjeldahl's Process. This depends upon the fact that the nitrogen in nearly all organic compounds is converted into ammonium sulphate when the substance is completely oxidised with strong sulphuric acid The ammonium sulphate is then decomposed by sodium hydroxide solution, and the ammonia, which is liberated, is distilled into an excess of decinormal sulphuric acid, the

unneutralised portion being subsequently determined by titration with decinormal sodium hydroxide The acid which has disappeared is exactly equivalent to the ammonia which has distilled over. From this the original nitrogen is calculated.

The process is carried out in the following manner A little of the substance to be analysed is accurately weighed A suitable quantity is from 0·2 to 1 gramme according to the percentage of nitrogen present This is then placed in a pear-shaped flask with a long neck (fig 37), of about 500 c.c. capacity About 20 c c of concentrated sulphuric acid is added, together with a fragment of copper foil or about 1 gramme of crystalline copper sulphate This is to serve as an oxygen carrier. The flask is then placed in an inclined position upon a piece of asbestos with a circular hole of about 1½ inch diameter, and heated gently, by a small Bunsen flame, with frequent rotation, till the substance has dissolved and frothing has ceased When solution is difficult to bring about, or much frothing occurs, it is advisable to carry out this part of the heating on a water-bath When solution is complete, the flame is turned up and heating continued till a clear, bluish solution is obtained The operation is conducted in a fume chamber, as much sulphur dioxide is evolved The inclination of the flask should be such that the sulphuric acid vapour is condensed on the sides and neck. After heating for about an hour, the mixture is allowed to cool somewhat and 5 grammes of powdered potassium sulphate are added. The heating is then continued If necessary, a second addition of sulphuric acid must be made also The potassium sulphate accelerates oxidation by raising the temperature of the reaction Of course, both sulphuric acid and potassium sulphate must be free from nitrogen When oxidation is complete, the mixture is allowed to cool It is then diluted with a little water, and, after cooling again, washed into a 250-c c flask, cooled, made up to the mark and mixed An aliquot part (*e g* 50 c c) of this solution is used for the determination This is placed in the round-bottomed flask shown in fig 38, together with a little powdered pumice to prevent bumping. Fifty c c of decinormal sulphuric acid are placed in the receiver, and the latter is connected as shown in the illustration Sufficient sodium-hydroxide solution to neutralise the acid in the flask is then placed in the tap-funnel. About 50 c c of a 40 per cent solution are generally sufficient The sodium hydroxide is then allowed to run into the flask The copper sulphate present serves as an indicator The mixture is now heated to the boiling-point and kept boiling for about seven minutes The receiver is then disconnected, its contents cooled and titrated with decinormal sodium hydroxide Cochineal solution is the best indicator for this titration From the volume of decinormal acid which has disappeared the percentage of nitrogen can be calculated, since each cubic centimetre of N/10 acid corresponds to 0·0014 gramme of nitrogen.



Fig 37.—Kjeldahl flask.

The sodium-hydroxide solution must be tested for ammonia by making a blank experiment If any is present it must be allowed for.

But pure caustic soda powder is generally quite free from nitrogen. The method of calculation is illustrated by the following example

0·5 gramme of a substance was Kjeldahled and made up to 250 c.c Fifty c c of this solution were distilled into 50 c.c. of decinormal acid. The volume of decinormal sodium hydroxide required to neutralise the distillate was 40·5.

Hence 50—40·5, *i.e.* 9·5 c.c. of decinormal acid have disappeared This is equivalent to $9{\cdot}5 \times 0{\cdot}0014$ gramme of nitrogen Therefore 250 c.c contain $9{\cdot}5 \times 0{\cdot}0014 \times 5$ grammes of nitrogen, *i.e.* 0·0665 gramme. Hence the substance contains $\frac{0{\cdot}0665}{0{\cdot}5} \times 100$, *i.e.* 13·3 per cent. nitrogen.

The Use of Assistants.—An oxidising agent or oxygen carrier is generally necessary In its absence the oxidation is very slow. Metallic mercury is often used, a small globule weighing about 0·5 gramme being introduced with the sulphuric acid The use of mercury introduces a complication, since, in its presence, mercuramines are formed which must be decomposed before distilling off the ammonia This may be accomplished by adding sufficient sodium or potassium sulphide (free from ammonia) to precipitate the mercury as sulphide Twenty c c of a 10 per cent solution are generally required Copper is an equally good oxygen carrier, and no amines are formed Almost any peroxidised compound, free from ammonia, may be employed, such as potassium permanganate or persulphate Perchloric acid is also said to be suitable and to reduce very greatly the time required for oxidation If oxidising agents are used, the first part of the oxidation is carried out with sulphuric acid alone. The following method is recommended by Gordon Parker (*J S C.I*, 1902, p. 838) in the case of leather From 0·5 to 0·7 gramme of the substance is heated with sulphuric acid for half an hour. The mixture is then allowed to cool and a dozen crystals of potassium permanganate are added The flask is again heated till a colourless solution is obtained. The Kjeldahl process requires close attention to detail The chief causes of errors are (1) insufficient digestion with sulphuric acid, (2) the presence of nitrogen in the reagents used; (3) inaccuracy of the standard solutions in titrating

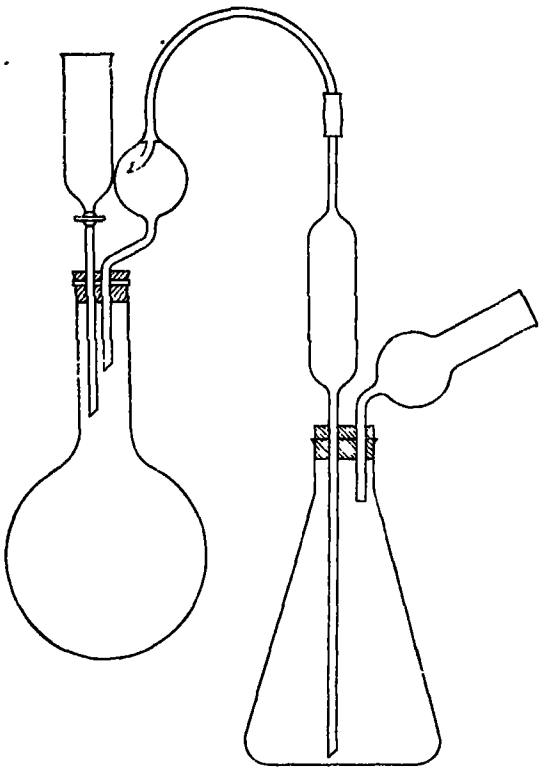


Fig 38.—Kjeldahl apparatus

In dealing with bulky substances like cotton, in which the percentage of nitrogen is also small, the manipulation of the Kjeldahl process is difficult. If a large weight of cotton be taken for analysis the oxidation is troublesome, while if only a small quantity be used the error of titration is considerable. The amount of nitrogen in 1 gramme of cotton does not require more than from 1·5

to 2 c c of decinormal acid for neutralisation. In such cases microchemical methods of analysis are useful Ridge (*J. Text Inst*, 1924, T. 94) gives the following as suitable for the estimation of nitrogen in cotton.—

1 **Titrimetric Method for Raw Cottons.**—One gramme of cotton in the pastille form, recommended by Williams, is covered with 6 c c. of concentrated sulphuric acid in a tube of resistant glass about 2·5 cm. in diameter and 19 cm. in length, 0·04 c.c. of mercury is added, the tube closed with a pear-shaped glass bulb, and the mixture heated over a low flame till it no longer shows any tendency to froth Two grammes of potassium bisulphate are then added and the liquid is boiled gently, without superheating the walls of the tube, until, in about three

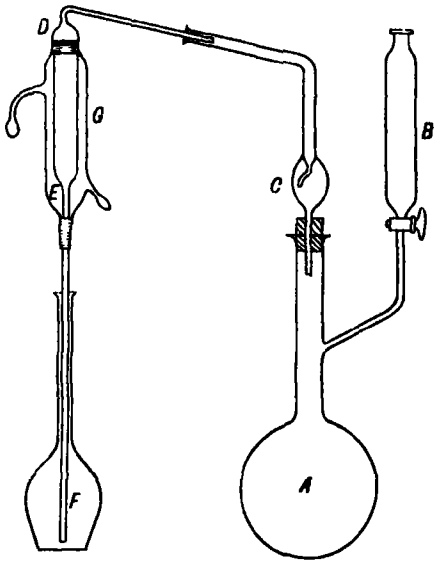


Fig 39.—Kjeldahl apparatus

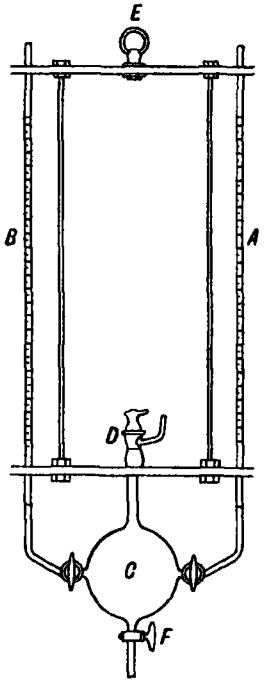


Fig 40.—Kjeldahl apparatus

hours, a clear, colourless liquid is obtained. After a further short period of boiling, to ensure complete digestion, the mixture is transferred to the hard glass distillation flask A (fig. 39), of 500 c c capacity, suitably diluted with distilled ammonia-free water to approximately 200 c.c, and the head-piece and delivery tube C, D, E, F are attached, after the addition of a few pieces of freshly ignited porous earthenware. The end of the delivery tube is inserted beneath the surface of an accurately measured volume (2 to 2·5 c.c) of decinormal hydrochloric acid contained in the titration vessel C (fig. 40), which replaces the vessel shown in fig 39. Sufficient 40 per cent. sodium hydroxide solution (35 to 40 c.c.) is added from the funnel B to render the contents of the flask alkaline, and finally 1·5 to 2 c c. of saturated sodium-sulphide solution. The ammonia is then distilled over, the rate of boiling being such as to yield 50 c.c. of aqueous distillate in about thirty minutes.

When this volume has been collected in the titration vessel, the distillation apparatus is removed, after washing the end of the delivery tube, and the excess of acid is titrated with decinormal sodium hydroxide free from carbonate, using methyl red as indicator It is necessary to carry out blank determinations at frequent intervals in order to correct the experimental result for the small quantity of ammonia which is invariably contained in the reagents, and for traces of alkali which may be carried over in the distillation For this purpose, 6 c c of sulphuric acid 0·04 c c of mercury and 2 grammes of potassium bisulphate are digested for three hours, transferred to the distillation apparatus, and the ammonia content determined in the manner already described The average correction is about 0·03 c c on the total titration of about 2 c c

The titration apparatus consists of two burettes, A and B, of 3 c c total capacity graduated in 0·01 c c These contain the standard acid and alkali respectively, and are sealed permanently to the titration bulb C in such a way that either solution can be admitted directly, in as small a volume as desired to the titrated liquid The capacity of the bulb is about 150 c c It is closed with a hollow ground stopper, through which connection with the air can be made when necessary, the whole apparatus being supported in a light framework on the neck D of the titration bulb The framework is suspended by the swivel ring E which enables the apparatus to be shaken during titration, and the bulb is washed out by means of the outflow tube and tap F The burettes can be read accurately to 0 002 c c , but must be carefully standardised and kept scrupulously free from grease. The form and quality of the head piece and delivery tube in the distillation apparatus C, D, E, F are of importance, both the extraction of alkali from the glass and the mechanical transfer of even very small traces of alkali during the distillation being sources of serious error Ridge from whose paper the above description is taken, uses a glass head piece C (fig 39) attached by means of a cork to a silica delivery tube D E F, with a widened portion D E which serves as a condenser and is surrounded by a glass water jacket G

In preparing the pastille mentioned above, Williams (*J Text Inst*, 1923, T 295), having weighed the cotton, compresses it into a plug in a screw pastille press

2 **Colorimetric Method for Bleached Cottons.**—Two grammes of cotton and 12 c c of sulphuric acid are used, the digestion and distillation being carried out in the same way as for the titrimetric method The microtitration apparatus is replaced by a 50 c c. measuring flask as shown in the figure Sufficient water is placed in the flask to cover the end of the silica tube and 40 c c of distillate are collected This is mixed with 7 5 c c of Nessler solution, made up to 50 c c , shaken and filtered immediately to remove a trace of metallic mercury which passes over with the distillate and interferes with the colorimetric comparisons At the same time two or more standards are prepared by diluting, for example, 2·5, 3, and 3 5 c c. of the standard ammonia solution to 40 c c , adding 7 5 c c of Nessler solution and making the volume up to 50 c c After all the solutions have been allowed to stand for ten minutes, that which appears closest in depth of colour to the solution for analysis is compared with it in a Kober Klett colorimeter, the concentrations of ammonia in the unknown solution being subsequently calculated on the assumption that the heights of columns of equal colour intensity are inversely proportional to the concentrations of ammonia in the Nesslerised solutions As in the titrimetric method blank experiments are necessary The following method of preparing Nessler solution is recommended. Two solutions are required

Solution A —Seventy-five grammes of potassium iodide are dissolved in

50 c c of warm water, 100 grammes of mercuric iodide are added, and the mixture stirred until the solution is complete It is then diluted with about 400 c.c. of water, filtered, and made up to 1 litre.

Solution B consists of a 10 per cent solution of sodium hydroxide free from carbonates and suspended matter

For the preparation of Nessler solution 200 c c of Solution B are added to 300 c c of Solution A and the mixture diluted to 1 litre.

The standard ammonia solution is made by dissolving 1·178 grammes of pure dry ammonium sulphate in 1 litre of water Each cubic centimetre of this solution is equivalent to 0·25 mgm of nitrogen.

The nitrogen content of raw cotton is given by Ridge as ranging from 0·2 to 0·3 per cent for American and Egyptian respectively The total nitrogen includes—

1. Protein nitrogen
2. Amino acid nitrogen
3 Nitrogen present in the natural colouring matters.

Higgins (*J Soc Dyers and Col*, 1919, p 165) showed that the whole of the protein and amino nitrogen could be removed from cotton by repeated boiling with sodium-hydroxide solution, but a residual 8·3 per cent could not be decomposed This must, therefore, be present in some more complex form.

CHAPTER VII.

OILS, FATS, AND WAXES; PECTOSE AND PECTIN COLOURING MATTER; MINERAL MATTER; TANNIC ACID.

Oils, Fats, and Waxes.

THE fatty constituents of cotton are complex in nature and include

(*a*) Glycerides
(*b*) Waxes
(*c*) Unsaponifiable oils
(*d*) Traces of soaps
(*e*) Traces of free fatty acids

Glycerides.— These compounds are the chief constituents of animal and vegetable oils and fats, and consist of triglycerides of fatty acids

The fatty acids are the monocarboxylic acids, derived from the paraffin series of hydrocarbons by replacing one atom of hydrogen by the carboxyl (—COOH) group They may be regarded, also, as oxidation products of the aldehydes or alcohols having relations to these similar to those of formic acid to methyl alcohol and formaldehyde These relationships are expressed in the following table

Paraffin	Alcohol	Aldehyde	Fatty Acid
$H.CH_3$	$H.CH_2OH$	$HCHO$	$HCOOH$
$CH_3.CH_3$	$CH_3.CH_2OH$	CH_3CHO	CH_3COOH
$C_2H_5.CH_3$	$C_2H_5CH_2OH$	C_2H_5CHO	C_2H_5COOH

The name fatty acids was given, originally, to this series because stearic and palmitic acids, the two commonest constituents of natural fats, are derived from paraffin hydrocarbons (general formula C_nH_{2n+2}) But it is more convenient now to use the term **Stearic Acid Series** The general formula of these acids is $C_nH_{2n+1}COOH$ Since they are derived from paraffin hydrocarbons, they are all "saturated," *i.e.* they cannot combine directly with bromine, hydrogen, etc , to form addition compounds. The lower members of the series are liquids, the boiling point of which increases gradually with the molecular weight Caprylic acid, $CH_3(CH_2)_6COOH$, is a solid, melting at 16·5° C. With the addition of each CH_2 group the melting point rises, stearic acid, $CH_3(CH_2)_{16}COOH$, melting at 69·3° C.

The more important members of this series are given in the following table —

Acid	Formula.	Occurrence
Butyric	$CH_3(CH_2)_2COOH$	Butter-fat.
Caproic	$CH_3(CH_2)_4COOH$	Cocoa-nut oil
Caprylic	$CH_3(CH_2)_6COOH$	Cocoa-nut oil
Lauric	$CH_3(CH_2)_{10}COOH$	Cocoa-nut and laurel oil
Palmitic	$CH_3(CH_2)_{14}COOH$	Most common fats
Stearic	$CH_3(CH_2)_{16}COOH$	Most common fats
Arachidic	$CH_3(CH_2)_{18}COOH$	Arachis oil
Lignoceric	$CH_3(CH_2)_{22}COOH$	Arachis oil
Cerotic	$CH_3(CH_2)_{24}COOH$	Beeswax and montan wax
Montanic	$CH_3(CH_2)_{26}COOH$	Montan wax
Melissic	$CH_3(CH_2)_{28}COOH$	Beeswax and montan wax

All of these fatty acids, from lauric acid upwards, are solids at ordinary temperatures, melissic acid melting only at 91° C Most of the solid fats consist, principally, of triglycerides of palmitic and stearic acids, together with smaller quantities of glycerides of the lower members of the series, to which they owe their special properties such as characteristic odour or flavour The fats are esters (or ethereal salts) of the trihydric alcohol glycerol, $C_3H_5(OH)_3$ An alcohol is, in some of its properties, similar to a base such as sodium hydroxide When sodium hydroxide is treated with an acid, *e g* acetic acid, sodium acetate is produced

$$NaOH+CH_3COOH=CH_3COONa+H_2O$$

If ethyl alcohol, C_2H_5OH, be treated with acetic acid in the presence of a little sulphuric acid a similar reaction occurs—

$$C_2H_5OH+CH_3COOH=CH_3COOC_2H_5+H_2O.$$

The compound thus produced is ethyl acetate, and is a typical ester. Ethyl alcohol is a monohydric alcohol, and, like sodium hydroxide, can only react with one molecule of a mono-basic acid. A metallic hydroxide containing two hydroxyl groups reacts with two molecules of a mono-basic acid, a trihydric base with three, thus

$$Ca(OH)_2+2CH_3COOH=2H_2O+(CH_3COO)_2Ca,$$
$$Bi(OH)_3+3CH_3COOH=3H_2O+(CH_3COO)_3Bi$$

Glycerol is, like bismuth hydroxide, trihydric, and hence can react with three molecules of acetic acid

$$C_3H_5(OH)_3+3CH_3COOH=3H_2O+(CH_3COO)_3C_3H_5$$

The ester thus produced is known as "triacetin" It is glycerol in which all three hydroxyl groups have been replaced by the acetyl group CH_3COO (or $C_2H_3O_2$) But the hydroxyl groups may be replaced successively, just as they may be in a trihydric metallic hydroxide giving monoacetin and diacetin Thus

$$C_3H_5(OH)_3+CH_3COOH=H_2O+(CH_3COO)(OH)_2C_3H_5,$$
$$C_3H_5(OH)_3+2CH_3COOH=2H_2O+(CH_3COO)_2(OH)C_3H_5,$$
$$C_3H_5(OH)_3+3CH_3COOH=3H_2O+(CH_3COO)_3C_3H_5$$

The esters, obtained from glycerol, are termed also "glycerides." When one hydroxyl group is replaced by a fatty acid radicle, the resulting ester is a

"monoglyceride" When two or three are replaced, the esters are termed diglycerides and triglycerides respectively

The solid fatty acids act in exactly the same manner as acetic acid Thus with palmitic acid, $C_{15}H_{31}COOH$, and stearic acid, $C_{17}H_{35}COOH$, we have mono-, di-, and triglycerides, which are termed palmitins and stearins, and are represented by the formulæ

Monopalmitin $C_3H_5(OH)_2C_{15}H_{31}COO$	Monostearin, $C_3H_5(OH)_2C_{17}H_{35}COO$
Dipalmitin $C_3H_5OH(C_{15}H_{31}COO)_2$	Distearin, $C_3H_5OH(C_{17}H_{35}COO)_2$
Tripalmitin, $C_3H_5(C_{15}H_{31}COO)_3$	Tristearin, $C_3H_5(C_{17}H_{35}COO)_3$

About 98 per cent of all natural fats consist of triglycerides, and, in the case of the solid fats, the triglycerides are principally tripalmitin and tristearin But triglycerides of other fatty acids than those of the stearic acid series also occur Thus, liquid oils and fats contain "triolein" derived from oleic acid, which belongs to another series The members of the remaining groups of fatty acids must therefore be described briefly

The Oleic Acid Series.—These acids have the general formula $C_nH_{2n-1}COOH$ The principal member is oleic acid $C_{17}H_{33}COOH$ It is liquid at ordinary atmospheric temperatures, its melting point being 14° C and solidifying point 4° C As indicated by its formula, it is an unsaturated compound, containing two atoms of hydrogen less than stearic acid the corresponding member of the saturated fatty acid series

The difference in the properties of oleic acid and the solid fatty acid series depends upon the fact that the former is unsaturated All fatty acids have certain properties in common They are insoluble or sparingly soluble in water, but are readily soluble in alcohol and such organic solvents as benzol, petroleum ether, and carbon tetrachloride Oleic acid can be distilled unchanged with superheated steam The saturated fatty acids distil also, but with slight decomposition All fatty acids burn when ignited with a smoky flame, and leave no ash When a fatty acid is treated with an alkali or an alkaline carbonate the corresponding salt is produced. Thus with sodium hydroxide or carbonate,

$$C_{15}H_{31}COOH+NaOH=C_{15}H_{31}COONa+H_2O,$$
$$2C_{15}H_{31}COOH+Na_2CO_3=2C_{15}H_{31}COONa+CO_2+H_2O$$

The metallic salts of the fatty acids are termed soaps (Chapter XIX) The soaps formed by the alkali metals and ammonium are soluble in hot water, those of the alkaline earths and heavy metals are insoluble The insoluble soaps may be prepared by treating a solution of a sodium soap with a salt of the heavy metal Calcium palmitate, for example, is obtained, as a white precipitate, when calcium chloride is added to a solution of sodium palmitate—

$$2C_{15}H_{31}COONa+CaCl_2=(C_{15}H_{31}COO)_2Ca+2NaCl$$

The soaps of the alkali metals and ammonium are not only soluble in hot water, but also in alcohol They are, however, as a rule insoluble in organic solvents Those of oleic acid are characterised by being comparatively soluble compared with the corresponding soaps prepared from saturated fatty acids Lead oleate is remarkable as being soluble in ether The properties of soaps will be described more fully in Chapter XIX

When oleic acid is exposed to the action of air and light, it becomes darker in colour and turns "rancid" This change is accompanied by the production of fatty acids of lower molecular weight When it is oxidised with a dilute alkaline solution of potassium permanganate, dihydroxystearic acid, $C_{17}H_{33}(OH)_2COOH$,

is first formed. Further oxidation converts dihydroxystearic acid into azelaic acid—

$$C_{17}H_{33}COOH+O+H_2O=C_{17}H_{33}(OH)_2COOH,$$
$$C_{17}H_{33}(OH)_2COOH+3O_2=2C_7H_{14}(COOH)_2+2H_2O.$$

When oleic acid is reduced with hydriodic acid it gives stearic acid—

$$C_{17}H_{33}COOH+2H=C_{17}H_{35}COOH.$$

From these facts it is known that it must contain one double linking between the carbon atoms in the molecule and have the formula

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH.$$

Oleic acid and other unsaturated fatty acids, or fats containing them, are reduced, also, when treated with hydrogen in the presence of a catalyst such as finely divided nickel, becoming changed into solid fats or triglycerides of saturated fatty acids. This process is used commercially in the manufacture of margarine and other edible fats.

Acids of the oleic acid series combine readily with two atoms of bromine or iodine, forming saturated dibromo or di-iodo compounds. Thus

$$CH_3(CH_2)_7CH=CH(CH_2)_7COOH+Br_2=CH_3(CH_2)_7CHBr.CHBr(CH_2)_7COOH.$$

This reaction forms the basis of the determination of the iodine value of fats.

Cold concentrated sulphuric acid changes oleic acid into a sulphonic acid, sulpho-oleic (or hydroxystearo-sulphuric acid), with the composition represented by the formula $C_{17}H_{34}(OSO_3H)COOH$.

The Linolic Acid Series.—These fatty acids have the formula $C_nH_{2n-3}COOH$, and contain two pairs of double-linked carbon atoms. They are thus more unsaturated than the acids of the oleic acid series.

Linolic acid, $C_{17}H_{31}COOH$, occurs in drying and semi-drying oils, such as maize and cotton-seed oil It is liquid at ordinary temperatures. When exposed to air it absorbs oxygen, and gradually forms a resinous skin or film consisting of hydroxy acids When oxidised with potassium permanganate in the presence of alkali it yields a tetrahydroxystearic acid, $C_{17}H_{31}(OH)_4COOH$. Linolic acid absorbs four atoms of hydrogen, bromine, or iodine.

Linolenic acid, $C_{17}H_{29}COOH$, contains three pairs of double linked carbon atoms, and hence absorbs six atoms of hydrogen, bromine, or iodine. It occurs chiefly in linseed oil, which dries readily when exposed to air, and is used, for this reason, as a vehicle for paints. When linolenic acid is oxidised it gives a hexahydroxystearic acid, $C_{17}H_{29}(OH)_6COOH$.

Ricinoleic Acid, $C_{17}H_{32}(OH)COOH$.—This acid is an important constituent of castor oil. It is a monohydroxy oleic and combines with two atoms of bromine. When oxidised with permanganate, it gives trihydroxystearic acid. Ricinoleic acid is of importance on account of its products of sulphonation. When treated with concentrated sulphuric acid a number of bodies are produced among which are ricinoleosulphuric acid, $C_{17}H_{32}(OSO_3H)COOH$; dihydroxystearo-sulphuric acid, $C_{17}H_{33}.(OH)(OSO_3H)COOH$. These sulphonated products are of considerable importance. Turkey-red oil is prepared by sulphonating castor oil.

The General Properties of the Triglycerides.

The triglycerides are either solids or liquids according to the proportion of saturated fatty acids which they contain. The term fat is used to denote a solid triglyceride, the name "oil" being reserved for those which are liquid at ordinary

temperatures. There are solid and liquid triglycerides of both animal and vegetable origin. This is indicated in the following examples —

1 **Animal Fats.**—Tallow, butter fat, lard.
2 **Vegetable Fats.**— Cocoa butter, vegetable tallow, palm oil
3. **Animal Oils.**—Fish oils, neatsfoot oil, whale oil
4. **Vegetable Oils.**—Seed oils, olive oil.

Oils and fats are generally colourless when pure. In some cases they have a greenish colour due to the presence of chlorophyll. The colour depends to a considerable extent on the method of preparation. Oils which are pressed out from tissues in the cold are generally nearly colourless, but if heat be used in the pressing, they are sometimes comparatively highly coloured Crude oils are often improved by bleaching.

The taste and odour of an oil is due to the presence of triglycerides other than tripalmitin, tristearin, or triolein Thus butter owes its distinctive flavour to esters of butyric acid

An unpleasant flavour is produced by impurities or by rancidity

All oils and fats are lighter than water, having a specific gravity of from 0·88 to 0·96 They are insoluble in water and generally, also, in alcohol, but dissolve readily in organic solvents such as ether, chloroform, carbon tetrachloride, benzol, or petroleum spirit Castor oil is an exception, in that it dissolves readily in cold alcohol and is only sparingly soluble in petroleum spirit When an oil is shaken with water, it is broken up into very minute particles, which form a temporary emulsion When the mixture is allowed to stand, these particles coalesce rapidly, and rise to the surface But, if soap be present, a comparatively stable emulsion is produced. Other colloids act in the same way (*vide* Chapter XIX)

When oils are heated to a temperature of about 250° C , they sometimes become thicker, and are said to be "polymerised," but the chemical changes which take place are not fully understood. The phenomenon is made use of in the preparation of lithographic varnishes Tung oil, heated to 250° C for a short time, changes into a jelly-like mass, while castor oil forms a substance like rubber in appearance

If the heating be continued, at a higher temperature, the oil becomes decomposed, various bodies being given off, including acrolein, C_2H_3 CHO, an aldehyde obtained from glycerol, which has an irritating effect on the eyes and a characteristic smell.

Many oils of the linolic and linolenic series, termed "drying oils," which contain unsaturated fatty acids, absorb oxygen, when exposed to the air, forming hard, solid films which contain hydroxy-fatty acids, and which are comparatively insoluble in organic solvents Oils may be classified as (1) drying oils, (2) semi-drying oils, (3) non-drying oils Examples are linseed oil (drying); cotton-seed oil (semi-drying), rape oil (non-drying)

It has been mentioned that oleic acid becomes rancid when exposed to air, this change being accompanied by the formation of free fatty acids, generally of lower molecular weight than those originally present Glycerol is also produced, and other bodies, including aldehydes, such as œnanthyl aldehyde, C_6H_{13}.CHO. Moist air is necessary for the production of rancidity, and it appears, also, to be connected with the action of enzymes A well-purified oil does not turn rancid as quickly as an impure one.

In addition to glycerides, all oils and fats contain a certain amount of free fatty acids. Liquid oils contain, generally, solid glycerides which separate out

gradually on standing, forming "foots." When oil is purified, it is kept at a comparatively low temperature for some time, and the "foots" are then removed by filtration, or by drawing off the supernatant liquid. Small quantities of cholesterol, $C_{27}H_{45}OH$, are always present in animal oils, while vegetable oils contain an isomer known as phytosterol. The identification of these alcohols is sometimes important, in deciding whether an animal oil is adulterated with a vegetable oil, or *vice versa*.

Triglycerides are decomposed, when heated under pressure with steam, into fatty acids and glycerol—

$$(C_{15}H_{31}COO)_3C_3H_5+3H_2O=3C_{15}H_{31}COOH+C_3H_5(OH)_3.$$

This process is used for the manufacture of both glycerol and fatty acids. The decomposition is much more rapid in the presence of a little sulphuric acid. Commercial "stearin" (which consists chiefly of stearic and palmitic acids), olein (oleic acid), and glycerol are made in the following manner: Tallow is decomposed by means of superheated steam at a pressure of about 15 atmospheres. The mixture is then allowed to stand till it separates into two layers. The lower aqueous layer contains the glycerol and is drawn off. The upper layer of fatty acids is pressed, in order to remove liquid oleic acid, the residue constituting stearin.

Fats are hydrolysed readily by Twitchell's reagent, which is a sulphonic acid, obtained by allowing excess of sulphuric acid to act on a solution of oleic acid in an aromatic hydrocarbon. Lewkowitsch gives the formula as $C_6H_4SO_3H$ $C_{18}H_{35}O_2$. About 1 to 2·5 per cent of this body hydrolyses fats completely, if they are heated in a current of steam, especially in the presence of some free fatty acid, which aids in starting the hydrolysis.

Fats can be hydrolysed, also, by means of fat-splitting (lypolytic) enzymes, which are present in many seeds and vegetable tissues. Castor oil contains such a ferment, termed "lipase." If an oil be mixed with water and from 6 to 7 per cent of lipase, about 90 per cent. of the fatty acids are liberated in forty-eight hours at ordinary temperatures. The oil cannot be decomposed completely, because the reaction is reversible, and a position of equilibrium is reached before hydrolysis is complete.

The Saponification of Fats.—All glycerides are decomposed when heated with a solution of a caustic alkali, with the formation of the metallic salt of the fatty acid and glycerol. This process is termed "saponification," and is the basis of the manufacture of soap (Chapter XIX.). In the case of sodium hydroxide and tripalmitin the reaction is

$$(C_{15}H_{31}COO)_3C_3H_5+3NaOH=3C_{15}H_{31}COONa+C_3H_5(OH)_3.$$

Although aqueous solutions of caustic alkalis may be used, saponification is much more rapid if an alcoholic solution be employed. Potassium hydroxide dissolved in alcohol is very largely used for this purpose in laboratories. The hydroxides of calcium, barium, and strontium are also able to effect saponification, but the soaps produced are insoluble in water—

$$2(C_{15}H_{31}COO)_3C_3H_5+3Ca(OH)_2=3(C_{15}H_{31}COO)_2Ca+2C_3H_5(OH)_3.$$

Saponification by means of both sodium hydroxide and calcium hydroxide is made use of in the purification of cotton (Chapter XVII.).

The Waxes.—The natural waxes are of both vegetable and animal origin. The former occur, chiefly, as "bloom" on the leaves or fruit of plants. Among animal waxes, spermaceti, beeswax, and wool wax are typical examples. The

waxes are, generally, solid at ordinary temperatures, and have much higher melting-points than the solid fats.

Waxes resemble oils and fats in that they are esters and are capable of being saponified, but the products of saponification are different. When a wax is saponified, no glycerol is obtained, but a monohydric alcohol, which has, as a rule, a comparatively high molecular weight. The other product of saponification is a fatty acid or a mixture of fatty acids, as in the case of the fats and oils.

Thus, a wax is not a glyceride, but an ester of a monohydric alcohol. Spermaceti may be taken as an example It consists chiefly of cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$ The radicle $C_{16}H_{33}$ (cetyl) gives rise to a monohydric alcohol, $C_{16}H_{33}OH$. When an ester is formed, therefore, only one molecule of the acid is required. Thus

$$C_{16}H_{33}OH+C_{15}H_{31}COOH=H_2O+C_{15}H_{31}COOC_{16}H_{33}.$$

Upon saponification with sodium hydroxide sodium palmitate and cetyl alcohol are formed—

$$C_{15}H_{31}COOC_{16}H_{33}+NaOH=C_{15}H_{31}COONa+C_{16}H_{33}OH.$$

The waxes differ from the glycerides, also, in the comparative difficulty with which saponification can be effected. The glycerides are all saponified when heated with aqueous sodium or potassium hydroxide, some even in the cold The waxes cannot, as a rule, be saponified by aqueous solutions of caustic alkalis. Prolonged boiling with alcoholic caustic potash is required and, sometimes, heating with a mixture of glycerol and sodium hydroxide, which is the most powerful saponifying agent known Thus, Knecht found that cotton waxes could not be decomposed with either aqueous or alcoholic potassium hydroxide.

Glycerides contain only traces of unsaponifiable oils Waxes, on the other hand, often contain true unsaponifiable oil, *i.e.* hydrocarbons

Like the glycerides, waxes are lighter than, and insoluble in, water. They are also soluble in organic solvents and form emulsions with soap and water

There are many monohydric alcohols which enter into the composition of natural waxes. The chief of these are given in the following table —

Name.	Formula.	Melting-point	Occurrence
		° C.	
Cetyl alcohol . .	$C_{16}H_{33}OH$	50	Spermaceti.
Octodecyl alcohol	$C_{18}H_{37}OH$	59	Spermaceti
Arachyl alcohol	$C_{20}H_{41}OH$	70	Fat of dermoid cysts
Ceryl alcohol	$C_{26}H_{61}OH$	79	Chinese wax
Melissyl alcohol	$C_{30}H_{61}OH$	88	Beeswax
Cholesterol .	$C_{27}H_{45}OH$	148–150	Animal oils
Isocholesterol . .	$C_{27}H_{45}OH$	137–148	Wool wax
Phytosterol	$C_{27}H_{45}OH$	135–148	Vegetable oils
Montanyl alcohol	$C_{28}H_{57}OH$	..	Cotton wax.
Gossypyl alcohol .	$C_{29}H_{61}OH$	82–88	Cotton wax.

A few waxes contain dihydric alcohols. Carnauba wax contains two, viz. carnaubyl alcohol, $C_{24}H_{48}(OH)_2$, and coccervl alcohol, $C_{30}H_{60}(OH)_2$, both of which are melting-points of 103° to 104° C.

The terms wax and oil are sometimes used wrongly. Japan wax and myrtle wax are not waxes but glycerides, giving glycerol and palmitic acid when saponified. On the other hand, sperm oil is a true wax, since it gives no glycerol but a monohydric alcohol.

Unsaponifiable Oils.—These oils, which are also known as mineral oil, consist of hydrocarbons. They are obtained, either by boring into petroliferous strata of the earth's crust, or by the distillation of coal, lignite, or petroliferous shale.

The chief kinds of hydrocarbon oils are—

1. Petroleum.
2. Shale oil.
3. Coal-tar hydrocarbons.
4. Lignite-tar oil.

Petroleum.

Crude petroleum is found in many parts of the earth, such as North America, Central America, Russia, Galicia, Persia, Borneo, and Burma. It is obtained by boring Artesian wells into the petroliferous strata. Sometimes the oil has to be pumped from the oil-bearing stratum, while, at others, it rises slowly without pumping or gushes out to a considerable height. In some districts, large quantities of natural gas are obtained, also, which are used for illuminating purposes or fuel. The origin of petroleum is a matter of speculation. It has been suggested that it was produced by the action of heat upon submerged deposits of either vegetable or animal tissues Another theory is, that it is derived from the fat of prehistoric sea animals. Either different causes or different starting-points have been involved, for the composition of crude petroleum differs considerably in different parts of the world.

The crude oil is a yellowish liquid which is lighter than water and which consists of a mixture of hydrocarbons.

American petroleum consists almost entirely of paraffin hydrocarbons of the series represented by the general formula C_nH_{2n+2}, but small quantities of benzene hydrocarbons are also present.

The paraffins present in American petroleum include—

Butane,	C_4H_{10},	boiling at	1° C.
Pentane,	C_5H_{12},	,,	38° C.
Hexane,	C_6H_{14},	,,	71° C.
Heptane,	C_7H_{16},	,,	99° C.
Octane,	C_8H_{18},	,,	125° C.

The paraffins from C_9H_{20} to $C_{16}H_{34}$ (boiling-point 270° C.) have been separated also, while others can be obtained by distillation up to 300° C.

The crude oil is separated into various fractions by distillation. These are—

(1) Petroleum ether,	boiling-point	40° to 70° C.
(2) Gasoline,	,,	70° to 90° C.
(3) Light petroleum or petrol,	,,	90° to 150° C.
(4) Kerosene (lamp oil),	,,	150° to 300° C.
(5) Lubricating oil and vaseline,	,,	above 300° C.

The residue in the retort consists of pitch.

Russian petroleum (or Caucasian) has a higher specific gravity than American petroleum; and contains a smaller proportion of hydrocarbons boiling

below 150° C. It differs from American petroleum in containing a large proportion of naphthenes or cyclic hydrocarbons, and also about 10 per cent of benzene hydrocarbons (C_6H_{2n-6})

The chief naphthenes present are octonaphthene, C_8H_{16}, and nononaphthene, C_9H_{18}

These can be made by the hydrogenation of benzene hydrocarbons

Thus xylene gives octonaphthene or xylene hexahydride—

$$C_8H_{10}+6H=C_8H_{16}$$

Russian petroleum contains also more solid hydrocarbons than the American, but yields less lubricating oil The paraffin waxes are separated from the residue after distillation and the fractions with high boiling points, by treatment with concentrated sulphuric acid and redistillation

Ceresine is the crude wax before redistillation It is used in cotton finishing as a softening agent

Galician petroleum is intermediate in composition between American and Russian Products similar to those from Russian petroleum are obtained also by the distillation of shale

Coal-tar hydrocarbons have the formula C_nH_{2n-6} They are obtained by the fractional distillation of coal tar (Chapter XX)

Hydrocarbon oils are unchanged by boiling with sodium hydroxide, alcoholic potash, or glycerol and caustic soda Hence they can be separated from glycerides and waxes by this means (p 67)

The paraffin hydrocarbons are saturated compounds and are not decomposed by acids Nor can they form addition compounds But when treated with chlorine they give rise to substitution products, hydrochloric acid being also formed Thus

$$CH_4+Cl_2=\underset{\text{methyl chloride}}{CH_3Cl}+HCl$$

Some chlorinated hydrocarbons are used as solvents and will be described in Chapter XX

Aromatic hydrocarbons react with sulphuric or nitric acid, forming sulphonic acids and nitro compounds respectively Thus

$$C_6H_6+H_2SO_4=H_2O+C_6H_5HSO_3 \text{ (benzene monosulphonic acid)}$$
$$C_6H_6+HNO_3=H_2O+C_6H_5NO_2 \text{ (nitrobenzene)}$$

They form, also, chlorine substitution compounds when treated with chlorine

$$C_6H_6+Cl_2=HCl+C_6H_5Cl \text{ (chlorobenzene)}$$

When hydrogenated, they combine with hydrogen, forming naphthenes or similar compounds some of which are important solvents (Chapter XX)

As indicated above, oils and fats contain small quantities of unsaponifiable oils, while waxes may contain a considerable proportion

The Quantity of Oil and Wax in Cotton.—The total amount of fatty matter removed by solvents from raw cotton appears to depend upon (1) the nature of the solvent used (2) the temperature of extraction, and (3) the physical condition of the cotton These points may be considered briefly

Petroleum ether, which is very commonly used in a laboratory, is a solvent of comparatively limited power Ether, benzene, carbon tetrachloride, and chloroform all extract more from cotton in the order given

Clifford, Higginbotham, and Fargher (*J. Text. Inst.*, 1924, T. 131), who made comparative experiments with different solvents, found that over a period of twenty-four hours the extraction may be divided into two periods During the first, extraction takes place rapidly, and measures, approximately, the matter readily soluble in the solvent; whilst, during the second, extraction proceeds at a much slower and diminishing rate over a long period, and appears to be concerned principally with matter of different characteristics soluble with difficulty in the solvent That is, the nature of the fatty matter extracted varies with the solvent and time of action. That different solvents remove different constituents has been shown already by both Knecht and Higgins. Clifford, Higginbotham, and Fargher also investigated the effect of the temperature at which the extraction is carried out The following table summarises their results —

		American Cotton Amount extracted (per cent.) in			
		1 Hour	4 Hours	16 Hours	32 Hours
Light petroleum (b.p. 40–60° C.)	cold	0·28	0·38	0·44	0·46
	hot	0·25	0·42	0·50	0·52
Light petroleum (b.p. 60–70° C.)	cold	0·34	0·44	0·47	0·48
	hot	0·42	0·48	0·50	0·52
Ether	cold	0·41	0·48	0·52	0·54
	hot	0·45	0·55	0·58	0·59
Benzene	cold	0·45	0·54	0·57	0·58
	hot	0·46	0·56	0·59	0·60
Carbon tetrachloride	cold	0·40	0·51	0·57	0·59
Chloroform	cold	0·52	0·60	0·62	0·63
	hot	0·67	0·76	0·78	
		Egyptian Cotton Amount extracted (per cent.) in			
		1 Hour	4 Hours	16 Hours	32 Hours.
Light petroleum (b.p. 40–60° C.)	cold	0·15	0·26	0·34	0·38
	hot	0·21	0·28	0·35	0·37
Light petroleum (b.p. 60–70° C.)	cold	0·27	0·35	0·40	0·43
	hot	0·35	0·37	0·41	0·43
Ether	cold	0·26	0·40	0·47	0·51
	hot	0·33	0·43	0·51	0·56
Benzene	cold	0·34	0·43	0·50	0·54
	hot	0·46	0·54	0·63	0·67
Carbon tetrachloride	cold	0·33	0·42	0·46	0·49
Chloroform	cold	0·49	0·57	0·62	0·65
	hot	0·52	0·61	0·68	0·72

These authors recommend that extraction of 100 grammes of cotton for a period of six hours with chloroform, in a hot Soxhlet apparatus, be adopted as a standard method for the determination of fat, wax, and resin in cotton, using a Soxhlet just conveniently large enough to contain the material and keeping the solvent actively boiling throughout the operation. They recommend the type of Soxhlet shown in fig. 41, made of sheet copper lined inside with tin.

It will be observed that the greatest percentage of extract obtained was 0·78 given by hot chloroform. Fort (*J. Soc. Dyers and Col.*, 1923, p. 44) gives much higher figures, but confirms the statement that a solvent with a higher boiling-point extracts more than one with a lower.

Knecht and Streat (*J. Soc. Dyers and Col.*, 1923, p 76) found that the quantity of matter extracted from cotton by organic solvents depends, to a certain extent, upon its physical condition, mechanical disintegration causing an increase in the matter soluble in benzol. In one experiment, some American raw cotton was extracted completely with benzol, giving 0·63 per cent. of extract It was then steeped in hydrochloric acid of 2° Tw strength for *fifteen* minutes, squeezed, dried, powdered, and again extracted with benzol. A further 0 39 per cent. of extract was obtained Higgins (*J. Soc. Dyers and Col*, 1923, p 150) had made similar observations, namely, that cotton contains some residual fat which cannot be extracted by solvents until it has been treated with acid. He showed, further, that magnesium was present in the acid solution, and concluded that magnesium soaps must be present in the cotton, which are decomposed when treated with acid with liberation of their fatty acids.

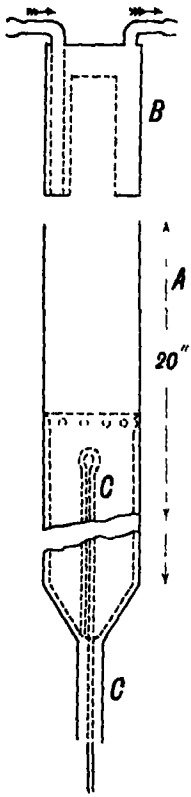


Fig 41 — Soxhlet apparatus

A, Soxhlet, B, condenser, C, syphon tube

The Composition of the Benzol Extract.— This was investigated by Fargher and Probert (*J Text. Inst*, 1923, T 49), who extracted 2 tons of American cotton with benzol for six hours They obtained 8 lbs of a dark brown semi-solid product which, after drying at 100° C *in vacuo*, gave a dark brown solid wax. This wax was extracted successively with light petroleum, ether, benzol, alcohol, and chloroform Extracts containing 60·7 per cent, 8·6 per cent, 12·8 per cent, 5·0 per cent, and 2·2 per cent respectively of the crude wax were obtained and submitted to detailed examination

The principal constituent was a new alcohol, $C_{30}H_{62}O$, which they term *gossypyl alcohol*. This appears to occur in three forms with melting-points of (1) 87° to 88° C, (2) 86° C, (3) 82° to 83° C. Other alcohols found were—

Montanyl alcohol, .	$C_{28}H_{58}O$.
Carnaubyl alcohol, .	. $C_{24}H_{50}O$
Sitosterol,	. . $C_{27}H_{46}O$
α- and β-amyrin,	. . $C_{30}H_{50}O$.

Among the acids isolated, palmitic, stearic, and oleic acids occur in the free state, the following chiefly as sodium salts montanic, cerotic, together with sodium palmitate and stearate, and the sodium salt of another acid with the formula $C_{34}H_{68}O_2$.

Esters included those of carnaubic acid, palmitic acid, stearic acid, oleic acid, but the proportion of unsaturated fatty acids is small. Two crystalline hydrocarbons, triacontane and hentriacontane, and other liquid hydrocarbons were isolated *No glycerol was found.* The composition of the various extracts and the relative importance of the constituents are shown by Fargher and Probert in the following table, substances present in large

amount being shown in black type, and those present in very small quantities in italics

Crude benzene extract

- **Light petroleum extract**
  - I Sparingly soluble.
    - **γ-Gossypyl alcohol, $C_{30}H_{62}O$**
    - **β-Gossypyl alcohol, $C_{30}H_{62}O$**
  - II Readily soluble
    - Free acids—palmitic, stearic, and *oleic*
    - Acids as esters—**carnaubic, $C_{24}H_{48}O_2$**, palmitic, stearic, and oleic
    - *Montanyl alcohol, gossypyl alcohol.*
    - *Solid hydrocarbons—triacontane, $C_{30}H_{62}$, hentriacontane, $C_{31}H_{64}$.*
    - **Liquid hydrocarbons**, b p 170° to 220° C 28 mm, and b p 150° to 210° C 1 mm
    - *Phytosterol*, $C_{27}H_{46}O$, principally sitosterol.
    - Amyrin, $C_{30}H_{50}O$
- **Ether extract**
  - III Sparingly soluble
    - **Montanyl alcohol, $C_{28}H_{58}O$**
    - *Sitosterolin*, $C_{33}H_{50}O_6$
    - *Palmitic acid*
    - *Stearic acid*
  - IV Readily soluble
    - Montanyl alcohol.
    - Palmitic acid
    - Stearic acid
- **Benzene extract**
  - V Sparingly soluble
    - **β-Gossypyl alcohol, $C_{30}H_{62}O$**
  - VI Readily soluble
    - *β-Gossypyl alcohol*
    - *Palmitic acid.*
    - *Stearic acid*
- **Alcohol extract**
  - VII Sparingly soluble
    - α-Gossypyl alcohol, $C_{30}H_{62}O$.
    - *Ceryl alcohol*
    - Sodium salts of montanic, cerotic, palmitic, and stearic acids
  - VIII Readily soluble
    - Sodium salts of fatty acids (united with similar material from sparingly soluble portion)
- **Chloroform extract**
  - IX
    - α-Gossypyl alcohol
    - *Carnaubyl alcohol*
    - An acid, $C_{34}H_{68}O_2$

It should be noted that the paper contains very full details of the chemistry and identification of these bodies. The chief interest in the fatty constituents of cotton centres on the waxes (This is because (1) they exercise an important effect in spinning, and (2) they are very difficult to remove completely in bleaching, (3) if not removed they tend subsequently to cause discolorations. These waxes were investigated first by Schunk, who found that the matter extracted from cotton by boiling alcohol could be divided into two distinct portions, soluble in the cold and boiling solvent respectively Both contained nitrogen, and included bodies now regarded as colouring matters)

A systematic investigation was carried out by Knecht and Allan (*J.S.C.I.*, 1911, p 813), who extracted cotton, successively, with petroleum spirit and benzol, proving also that the wax could be obtained in two portions with different solubilities. That soluble in petroleum spirit was an odourless, dull yellow substance closely resembling beeswax in appearance, texture, and fracture. When treated repeatedly with boiling 96 per cent. alcohol an insoluble residue (18·82 per cent) of a glassy wax was obtained, melting at 78° C. The portion soluble in alcohol was more plastic, it melted at 62° C , and had an iodine value of 33 compared with 11·28 in the case of the insoluble wax. The wax could only be completely saponified by heating with glycerol caustic soda, and gave 47·5 per cent. of unsaponifiable matter melting at 67° to 68° C. After acetylation, a phytosterol was identified, and two hydrocarbons whose composition agreed with

those of hentriacontane, $C_{31}H_{64}$, and dicetyl, $C_{32}H_{66}$. Small quantities of glycerol, cerotic, stearic, and palmitic acids were also obtained from the soap solution. The second fraction of the wax extracted by benzol was a dark green granular mass melting at 68° C. After acetylation it gave also a phytosterol, and a fatty acid which was probably melissic acid, $C_{30}H_{60}O_2$. The crude wax soluble in benzol obtained from Egyptian cotton and amounting to 0·47 per cent was studied further by Knecht (*J.S C.I.*, 1911, p. 1007). When treated with petroleum spirit, it is resolved into two portions which he terms cotton wax A and B Cotton wax A is that portion soluble in petroleum spirit It amounts to 70 per cent It has a pale yellow colour, melting at 66° to 67° C., and consists chiefly of a true wax, containing also some free fatty acids, a little glyceride, and some unsaponifiable hydrocarbons Cotton wax B, insoluble in petroleum spirit, is a dark green granular plastic substance melting at 68° C. In a more recent paper (Knecht and Streat, *J. Soc. Dyers and Col.*, 1923, p 73), it is shown that the crude cotton wax of Knecht and Allan contains also the cotton wax (m p. 86° C.) described by Schunk, and also another white solid with similar appearance and properties, but melting at 79·5° to 80° C For these the names white cotton wax α and white cotton wax β are suggested

White cotton wax α is obtained from cotton wax B of Knecht and Allan, and also from that portion of the crude cotton wax which is insoluble in cold benzol. It would appear, therefore, to be less readily soluble than white cotton wax β, which is obtained from the portions of both the crude wax and cotton wax A, which dissolve in cold benzol The crude cotton wax already separated by Knecht and Allan was first exhausted with petroleum spirit. The solution upon evaporation gave cotton wax A. The residue was extracted with benzol to remove wax B Ten grammes of wax A were lixiviated with small quantities of boiling alcohol till no further solution was effected. The insoluble residue (1·585 grammes or 18 85 per cent) had a dark brown colour and was not examined further. The alcoholic solution was filtered whilst hot and the filtrate cooled. A brownish solid separated, having a melting-point of 68° to 69° C. This was dissolved in methyl alcohol, the solution boiled with animal charcoal and filtered On cooling the filtrate, a wax-like solid separated with a faint yellow colour and melting at 79° C The yield was 9·4 per cent This was named " white solid D." When treated similarly, cotton wax B gave 20·05 per cent of residue insoluble in alcohol, the filtrate yielding a yellowish substance melting at 84° C This, after purification with methyl alcohol and charcoal, gave a white waxy solid melting at 86° C , which was named wax C. Probably A and C are identical, and also B and D. The white solid D appears to be unsaponifiable Thus Knecht and Allan's crude wax contains (1) Schunk's wax, m p. 86° C , and (2) a white solid, m p 79·5° to 80° C , or white cotton wax α and β.

In a later paper by Clifford and Probert (*J. Text. Inst.*, 1924, T. 401) these experiments were repeated on American Mississippi Delta cotton The wax was, in this case, extracted by means of chloroform, which was used in preference to the 90 per cent benzol employed in the previous experiments for the following reasons (1) the heating was by the introduction of superheated steam, causing possibly saponification of some of the esters; and (2) the benzol was impure.

The following table summarises the properties of the waxes obtained from the Delta cotton and from the Upland cotton, used in the previous experiments, by extraction with carbon tetrachloride for six hours. The results obtained confirm those recorded before, except that hydrocarbons were introduced by the impure benzol.

	Mississippi Delta Cotton	American Upland Cotton
Wax per cent. on dry cotton	0·49	0·35
Melting-point	76 5° C.	80 5° C.
Density	0 976	1 005
Acid value	29	21
Saponification value	57	76
Saponification value after acetylation	137	121
Acetyl value	84	48
Iodine value	27	20
Unsaponifiable matter	68 per cent	66 per cent.
Acetyl value by unsaponifiable matter	123	117

The wax of Mississippi Delta cotton contains, evidently, a lower proportion of combined acids and a somewhat higher proportion of free alcohols than the Upland cotton, though the higher acetyl value of the former is probably accounted for, in part, by the larger amount of sitosterol glucoside which has been shown to be present

The following substances were identified —

1 **Alcohols.**—These include—

Gossyppyl alcohol and *montanyl* alcohol, which are the chief constituents. Smaller amounts of alcohols, $C_{34}H_{70}O$ and $C_{32}H_{66}O$, and a mixture of glycols, $C_{30}H_{66}O_2$ and $C_{28}H_{58}O_2$, were also found.

Sitosterol, $C_{27}H_{46}O$, α- and β-amyrin, $C_{30}H_{50}O$, lupeol, $C_{31}H_{50}O$

A new sterol, $C_{34}H_{58}O$, and a glucoside of sitosterol (sitosterolin)

Lupeol occurs fairly widely distributed in the vegetable kingdom, having been first isolated from the seed part of *Lupinus luteus* by Likiernik, who assigned to it the formula $C_{26}H_{42}O$, but Cohen suggested $C_{31}H_{50}O$ The sterol, $C_{34}H_{58}O$, has not been described before.

2 **Acids.**—The free acids consisted principally of palmitic and stearic acids Smaller amounts of carnaubic acids were found also, and very small quantities of *gossypic* and *montanic* acids, oleic acid, and the acids $C_{34}H_{68}O_2$ and $C_{32}H_{64}O_2$. Palmitic acid, oleic acid, stearic acid, carnaubic acid, and small amounts of the higher acids (including melissic) occur as esters in combination with glycerol and phytosterols Carnaubic acid appears to exist in combination with phytosterols, and the higher acids with wax alcohols No soaps were found, and it would seem that the existence of these in the earlier benzene extract was due to the method of extraction used It should be noted that glycerol was definitely identified.

3. **Hydrocarbons**, mainly liquid, were present in small amounts, and a trace of a solid hydrocarbon, probably heptacosane Resinous substances of a complex nature were separated also

The Effect of the Cotton Waxes on the Spinning Properties.—Knecht (*J. Soc. Dyers and Col*, 1918, p 220) proved that cotton wax exercised an important effect in spinning Egyptian cotton, after extraction, gave, when spun, excessive waste and irregular results It showed a tendency to adhere to the rollers, and, in spinning fine counts, breakages were frequent. The yarn, after spinning, was from 24·5 to 27 per cent. weaker in tensile strength than ordinary yarn of the same count When used for warps in weaving, breakages were frequent But if the yarn was spun in the ordinary way, and then degreased with benzol, it was found to be 13 per cent stronger after degreasing The addition of 2 per

cent. of paraffin wax to the wax-free yarn decreased its tensile strength by 33 per cent American yarn increased in strength to the extent of 12·4 per cent. when extracted with benzol, but lost 4 per cent in elasticity. Higgins (*Bleaching*, p. 15) obtained different results for linen yarns. These are seen in the following table.—

	Breaking Strength in Grammes
Original yarn	730
After ether extraction	790
After benzol extraction	750
After alcohol extraction	720

The ether evidently removed matter which caused the slipping of the fibres over one another, and benzol, apparently, extracted waxy matter which had a solidating effect on the fibres In this and other tests the greatest increase in strength was always produced by the solvent with the lowest boiling-point, viz ether. Founded upon his experiments, Knecht has patented a process for treating cotton with an organic solvent to facilitate spinning. The object of the process (*J Soc Dyers and Col*; 1923, p 183) is to soften rather than to extract the waxy impurities, and is applied to cotton after opening out and partial cleaning prior to carding The method of procedure consists of placing the cotton in a closed vessel into which a current of air laden with the vapour of a suitable solvent is introduced in such a way as to saturate the air in the vessel without coming into contact with the cotton. Such solvents as naphtha, petroleum, turpentine, or tetrachlorethane may be employed. The vessel used is provided with a porous lining or porous pipes, which permit of more or less rapid vaporisation, though the treatment may be carried out also in an opening machine such as a bale breaker or scutcher

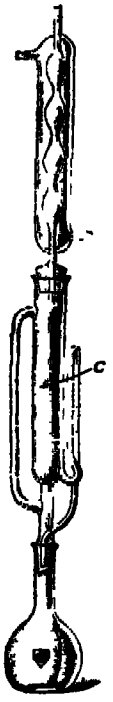


Fig 42 — Soxhlet extractor

The complete removal of cotton oil and wax constitutes the chief difficulty in cotton bleaching Oils can be removed from textile materials in three ways, viz (1) by saponification, (2) by emulsification with soap, (3) by extraction with an organic solvent The third method is the only one that ensures absolute freedom from oil and wax, though the other two are more commonly employed These points will be discussed fully later (Chapter XVII).

The Estimation of Oil and Wax.—The experiments of Fargher and Probert have been described above. Two types of fat-extraction apparatus are commonly used, viz. (1) the Soxhlet extractor, and (2) the continuous extractor A Soxhlet extractor is illustrated in fig 42 A weighed quantity of dry material is placed in the extracting chamber A, while rather more of the solvent than is required to fill the chamber to the top of the syphon B is placed in the flask C, which has been previously weighed The flask and Soxhlet are then connected with a vertical condenser as shown in the figure The solvent is then gently boiled by means of a water-bath or a small flame according to its boiling-point. The vapour of the solvent, following the line of least resistance, passes up the wide side tube D into the chamber, is condensed by the condenser and drops back into the extracting chamber As soon as the level of the condensed solvent rises above the top of the syphon tube B, the solvent runs back into the flask

and the operation recommences. As a rule about three hours are required to complete the extraction, provided that the solvent is continuously boiled The flask is now removed, the solvent evaporated off, and the residue dried in a steam-oven and weighed. The disadvantage of this process is, that the solvent in the extracting chamber is comparatively cold Extraction with a hot solvent is, as noted above, more rapid and efficient. The type of Soxhlet illustrated in fig. 42 provides for this. But as a rule it is more convenient to employ a " continuous "

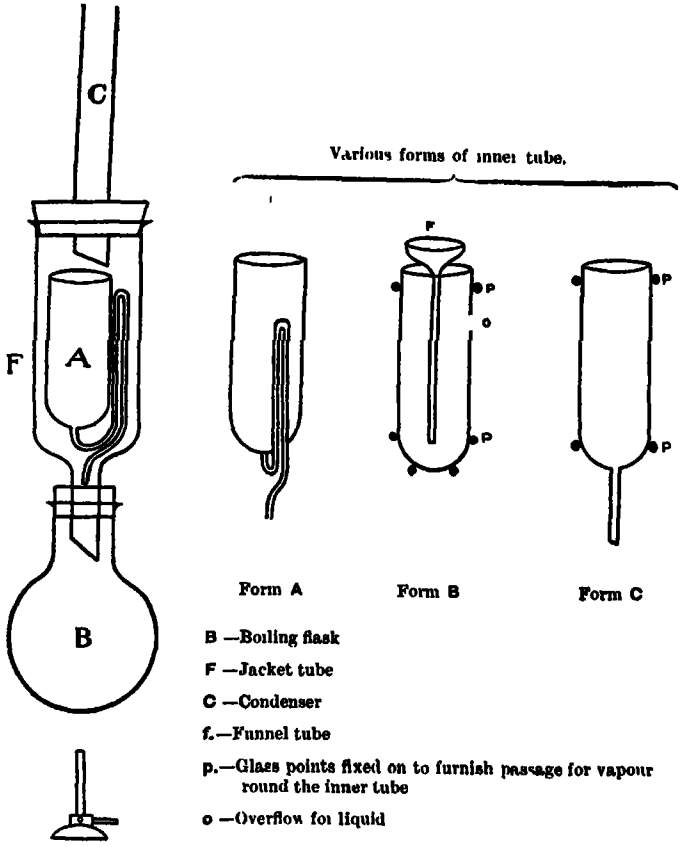


Fig. 43 —Lloyd's extractor

extractor if hot extraction is desirable. Lloyd's extractor, illustrated in fig. 43, is both simple and efficient.

The material to be exhausted is placed in the inner chamber A, which rests upon glass projections B to allow of the passage of the vapour. The solvent is placed in the flask C and kept boiling fairly rapidly. The vapour condenses and drops into the inner chamber A. Since this is surrounded by hot vapour, continuous extraction with the solvent at a temperature near its boiling-point is obtained. The material must be packed carefully in the inner chamber in order to avoid channels through which the condensed solvent could percolate.

Pectoses and Pectins.—Pectose, $(C_6H_{10}O_5)_n$, is a colloidal carbohydrate belonging to the cellulose group (Chapter VIII.). It is found associated with

cellulose in plant tissues and, particularly, in unripe fruits. It is present in the cell wall of the cotton hair together with its derivatives pectin and pectic acid. Pectose is an insoluble colloidal substance, but differs from cellulose in being readily hydrolysed by prolonged boiling with water or alkalis, or by the action of enzymes

The first product of hydrolysis is "pectin," which may have the composition $C_{32}H_{40}O_{28}$, or, according to Schryver and Haynes, $C_{17}H_{24}O_{16}$. The hydrolysis of pectose into pectin is brought about, in nature, by the action of a ferment termed "pectase" In an unripe fruit much pectose is present. As ripening proceeds, this pectose is transformed into pectin by the action of pectase Thus, ripe fruits contain much pectin and comparatively little pectose Irish moss consists largely of pectin, while apples and gooseberries contain a large proportion The pectins are insoluble in cold water, but gradually form colloidal solutions when boiled with water These set to a jelly on cooling. Pectin is precipitated from its solutions by basic lead acetate When boiled for some time with water, or alkalis, it is changed into bodies known as metapectin and parapectin Prolonged boiling of pectins with water or dilute alkalis, or the further action of enzymes changes them into "pectic acid," $C_{16}H_{22}O_{15}$ Pectic acid is, like pectin, a colloidal substance which is insoluble in cold water but forms a colloidal solution in boiling water, which sets to a jelly on cooling Pectic acid forms salts with metals Those of the alkali metals are soluble in hot water, but the pectates of calcium and magnesium are insoluble If an acid be added to a solution of a pectate, insoluble pectic acid is precipitated in the form of a jelly When pectic acid is boiled for a long time with either dilute acids or alkalis it gives metapectic acid This acid is no longer colloidal. It dissolves readily in water and forms soluble salts Its solutions do not set when cold, nor is the acid precipitated when metapectates are treated with a mineral acid All of these changes are also brought about by the action of pectase, and take place simultaneously Thus pectoses, pectins, and pectic acids are found, commonly, together as in the cotton hair Prolonged boiling with sodium hydroxide, however, converts all three kinds into soluble non-colloidal metapectic acid

Barnes (*J S C I*, 1916, p 1194) states that the presence of large and varying amounts of carbonates in the ash of cotton fibre leads us to suppose that some portion of the mineral matter is present in combination with an organic acid. Pectin and salts of pectic acid play an important part in forming the binding substances between plant fibres They have been shown by Mangin to consist of three classes of substances—

(*a*) Neutral bodies including pectose which are insoluble in water and resemble cellulose.

(*b*) Neutral bodies of a gelatinous nature soluble in water and known as pectins.

(*c*) Faintly acid substances such as pectic acid which occurs chiefly as calcium pectate Such acids will account for the absorption of some of the mineral matter, and indeed neutralisation of excessive acidity may be one of the functions of alkaline salts in cell sap.

The nature of the pectins is still indefinite. Different observers do not agree even as to its percentage composition Cross and Bevan (*Cellulose*, p. 217) classify the pectins as carbohydrates containing acid groups. But they seem to contain more oxygen and less hydrogen than the carbohydrates, and their acid properties become more marked on hydrolysis. Schryver and Haynes

(*Biochem Jour*, 1906, **10**, 539) are of opinion that pectins are not carbohydrates but acids

The Mineral Constituents of Cotton.—The quantity, and nature, of the mineral constituents of the cotton hair vary with the composition of the soil in which the plant grows and also with the kind of cotton Certain elements are essential to plant life In addition to carbon, hydrogen, nitrogen, oxygen, and sulphur, the invariable constituents of proteins, phosphorus, calcium, magnesium, potassium, and sodium, and iron, are also necessary Silica is required to give rigidity to the hard tissues Other elements, such as iron and aluminium, may also be present, but are not essential to the formation of protoplasm But a plant cannot select the saline bodies which it takes up Whatever soluble diffusible salts the soil contains will be taken up with the water which enters through the root hairs This is evaporated again at the surface of the leaves, the soluble salts being left behind in the plant tissues Thus the mineral constituents, beyond the essential ones, must be determined to a certain extent by the soluble salts which are present in the soil The exact nature of these mineral salts in the plant cannot be determined directly All that can be done is to burn the tissue to an ash and weigh and analyse this Having determined the acids and bases which it contains one can recombine these according to their chemical affinities and thus reconstruct their probable combinations in the plant tissue. There is however, one difficulty Some of the bases are combined with organic acids Thus calcium occurs probably as calcium pectate When the calcium or sodium salt of an organic acid is incinerated sodium or calcium carbonate is produced Hence the presence of carbonates in the ash may indicate merely that the calcium was combined originally with an organic acid Cotton lint may contain, in addition to the natural mineral constituents of the hair, such extraneous mineral matter as sand and dirt

The following table gives the percentage of ash found in different varieties of cotton lint by Matthews and Monie respectively

	Matthews	Monie.
Dharwar	4 16	
Dholleiah	6 02	4 10
Sea Island	1 25	1 10
Peruvian soft	1 68	1 80
Peruvian rough	1 15	1 25
Bengal	3 98	5 30
Broach	3 14	2 58
Omrawuttee	2 52	2 93
Egyptian brown	1 73	1 60
Egyptian white	1 19	1 75
Pernambuco	1 60	1 98
American	1 52	1 60 2 10

The present authors have determined the percentage of ash given by a number of different varieties of cotton of known origin and purity The results are recorded in the following table —

Variety of Cotton.	Percentage of Ash
American .	1 19
Brown Egyptian	1 93
Sea Island .	0 99

Variety of Cotton	Percentage of Ash
Peruvian	2 46
Brown Sudan	1 39
Soudan	3 91
Ceara	2 00
West Indian	1 44
Nyassaland	1 59
Surat	1 59
Uganda	1 76
China	1 01
West African	2 12

Barnes (*J S.C I.*, 1916, p 1191), who has paid particular attention to the determination of mineral matter in cotton, gives the following figures

Variety of Cotton	Percentage of Ash
Texas	1 27
Memphes	1 92
Arkansas	1 33 -1 67
Sea Island	1 18
Brown Egyptian	1 37
Indian	1 34–3 99

It will be noted that the ash content may rise to 3·99 per cent in the case of Indian cottons Barnes concludes that the total ash in cotton fibres has been underestimated by previous workers, who have assumed that it was largely due to foreign mineral matter in the form of dirt in the baled cotton He considers it established, that genuine cotton may contain upwards of 1 per cent of ash, and that the composition of this ash is variable to a greater extent than hitherto supposed The ash content of cotton may easily be underestimated owing to the fact that it contains sodium and potassium chlorides which are lost unless the ignition is carried out at a low temperature The colour of the ash of cotton varies from white to grey, brown, or reddish brown It is always strongly alkaline to phenolphthalein, and contains a considerable quantity of carbonate In general, it consists of aluminium, calcium, magnesium, sodium, potassium, and sometimes iron, combined with chlorine, sulphuric, phosphoric, silicic, and carbonic acids

Matthews (*Textile Fibres*, p 212) gives the following percentage composition of the ash —

	Ure	Davis, Dreyfuss, and Holland
Potassium carbonate	44 8	33 22
Potassium chloride	49 9	10 21
Potassium sulphate	9 3	13 02
Sodium carbonate	.	3 35
Calcium phosphate	9 0	
Calcium carbonate	10 6	20 26
Magnesium phosphate	8 4	8 73
Magnesium carbonate	..	7 81
Ferric oxide	3 0	3 40
Aluminium oxide and loss	5 0	

In the case of Indian cottons the following figures are given by Barnes (*loc cit*)

	Amble Guzerat, Bombay	Chiniot Road, Punjab
Silica insoluble in HCl	15 56	14 40
Alumina	10 80	12 87
Iron oxide	5 89	1 92
Lime	9 75	10 65
Magnesia	1 87	4 36
Sulphates (as SO_4)	1 96	2 52
Phosphorus pentoxide	3 26	4 46
Potash	27 32	26 03
Chlorine	6 55	3 84
Carbon dioxide	12 19	8 03
Soda	4 51	8 40
Undetermined and loss	0 34	2 52

Yarns and piece goods may contain much more mineral matter than cotton fibre, including such bodies as magnesium and zinc chlorides used in the preparation of sizing mixtures But, as a rule, the ash of a prepared cotton has much the same composition as that of the cotton fibre and does not often exceed 1 per cent in amount

It will be noted that many of the mineral constituents of cotton are soluble in water, while practically everything except the silica can be removed by hydrochloric acid

Knecht and Hall (*J S C I*, 1919, 7A) found that a considerable quantity of mineral matter, consisting chiefly of potassium salts, was extracted by alcohol from both American and Egyptian cotton

Geake (*J Text Inst*, 1924, T 81) proved that the various growths of trade cottons have characteristic phosphorous contents, and this fact may be used in certain cases to distinguish between them For example no difficulty was experienced in distinguishing with certainty between American and Egyptian growths

The average values are approximately as follows .—

American	0 05 per cent	P_2O_5
Sea Island	0 07 ,,	,,
Sakellaridis	0 12 ,,	,,
Egyptian and other Sakellaridis	0 09 ,,	,,
South American	0 07 ,,	,,

Raw cotton direct from the bale has an irregular phosphorous content due to lack of uniformity in the material, but no irregularity was observed in cotton at any stage of the manufacturing operations For the estimation a sedimentric method is recommended, in which the phosphoric acid is precipitated with strychnine molybdate and measured after centrifuging in a graduated tube, the volume of the precipitate being compared with that obtained under identical conditions from a known weight of phosphoric acid

It was observed, also, by Geake that the phosphorous content of the various classes of cotton followed their power of absorbing methylene blue It is well known that unremoved mineral matter may alter the affinity of a textile fibre for dyestuffs

The Removal of Mineral Matter.—Except for special purposes, mineral matter is only removed incidentally in bleaching. The ash of bleached cotton is usually about 0·1 and rarely exceeds 0·5 per cent. The bulk of it consists of unremoved calcium compounds introduced by the bleaching liquor. Where greater freedom from mineral matter is required, the bleached cotton is treated with hydrochloric or hydrofluoric acid and washed. It is impossible, however, to make ash-free cotton or cellulose by any known means, though the ash content may be reduced to very small proportions. Part of the mineral matter is soluble in water, still more may be removed by treatment with dilute hydrochloric acid, while nearly all of it is dissolved by boiling with dilute sodium hydroxide under pressure The lye boil is, in effect, the chief process which removes mineral matter. But little, if any, is removed afterwards. On the contrary, the ash content is generally increased by the subsequent bleaching, unless sodium hypochlorite is used

The following figures show the effect of the ordinary processes of the bleaching :—

	Percentage of Ash	
	Exp 1	Exp 2
Original yarn	1 17	0 94
After boiling with 2 per cent sodium hydroxide under pressure	0 02	0 006
After bleaching	0 02	0 006

It will be noted that practically all of the mineral matter is removed by the soda-boiling process, provided, of course, that the subsequent washing is thorough It has been shown by Trotman and Pentecost that mineral matter inhibits or retards the hydrolytic action of sodium hydroxide on the fats and nitrogenous constituents of cotton If the cotton is charged with unremoved saline constituents, when it is boiled with alkali this retarding action is produced, and incomplete removal of other impurities may result This can be avoided by taking advantage of the fact that much of the mineral matter can be removed by a preliminary soak in water or dilute hydrochloric acid This is seen from the following figures :—

	No 1	No 2
Ash in original yarn	1 17	0 94
Ash after soaking in water	0 26	0 27
Ash after soaking in warm hydrochloric acid at 1 Tw	0 08	0 13

This point will be referred to again later when dealing with the process of steeping One point, however, is evident If an ash-free cotton is required, the proper course is to remove the mineral matter by preliminary washing with acid, instead of from the bleached goods as is generally done

Colouring Matters.—The proteins, waxes, and pectins of the cotton hair are all more or less coloured Removal of these naturally reduces the colour. But these coloured impurities are all removed by boiling the cotton with sodium

hydroxide and washing the residue with water. When this has been done there remains still a residuum of colour which can only be removed by bleaching. This residuum is the "natural colour principle." It is in some way associated with the cell protoplasm and is itself nitrogenous. It varies in amount in different varieties of cotton, being greatest in brown Egyptian cotton. The colouring matter of cotton cannot be removed by any one solvent, but is partly soluble in many, such as water, alkalis, alcohol, benzene, etc. Knecht found that the extracts obtained successively with benzol, alcohol, water, and ammonia were all coloured Benzol extracts much colour. The alcoholic extract, after removal of the benzol soluble constituents, has a rich brown colour, and upon evaporation yields a brown hygroscopic amorphous substance The aqueous extract gives brittle brown scales, while still more colour is removed by water and ammonia. These colouring matters were studied first by Schunk, who concluded that in American and East Indian cotton it was of two kinds, one soluble in cold, and the other in boiling, alcohol, and both containing nitrogen. They were difficult to investigate since they were uncrystallisable and resinous. The percentage of nitrogen found was 6·18 for that soluble in cold, and 8·74 for that soluble in boiling, alcohol. Schunk's colouring matter probably included cotton wax Knecht has recently isolated compounds which he regards as the true colouring matters. They are destroyed by oxidising agents such as chlorine, hypochlorous acid, or peroxidised compounds, and form leuco-compounds with reducing bleaching agents such as sulphur dioxide.

The natural residual colouring matters are comparatively easy to remove by bleaching after complete removal of the cotton waxes, proteins, and pectins. In cotton bleaching, the processes are designed to render soluble, and remove by washing, all of these impurities before subjecting the goods to the bleaching operation The purity and durability of the final colour is largely determined by the completeness of these preliminary processes

Tannic acid, $C_{14}H_{10}O_9$, is distributed very widely in vegetable tissues. Galls consist largely of "tannin," which is probably a glucoside of tannic acid The dried leaves of the sumac tree contain 25 per cent. of tannic acid, and many other leaves, barks, and woods contain it in considerable quantities. It can be extracted from materials containing it by extraction with water.

Pure tannic acid is a colourless amorphous substance, readily soluble in water and alcohol, but only very slightly soluble in ether Its aqueous solution has an astringent taste, and weak acid properties. It forms salts with metals. Those of the alkali metals are soluble in water, but tannates of heavy metals are insoluble Its solutions in sodium hydroxide absorb oxygen when exposed to the air and become brown in colour When a solution of tannic acid is treated with a soluble iron salt, such as iron alum, a deep blue-black or green-black colour is produced This reaction is made use of in the preparation of ink, while insoluble tannate of iron is produced in silk for the purpose of weighting Tannic acid combines with many organic bases giving insoluble salts. Some alkaloids and all basic dyestuffs can be precipitated from their solutions as tannates, and tannic acid is used as a mordant for cotton when it is dyed with basic dyestuffs.

The most important property of tannic acid is its power of forming an insoluble compound with gelatin and proteins, which is the basis of the manufacture of leather.

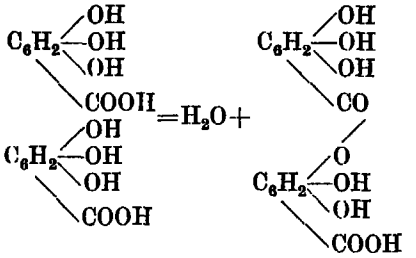
When tannic acid is boiled with a dilute acid it is hydrolysed into gallic acid, $C_6H_2(OH)_3COOH$—

$$C_{14}H_{10}O_9+H_2O=2C_7H_6O_5.$$

If gallic acid be heated to a temperature of 210° C. it gives off carbon dioxide and leaves a residue of pyrogallol, $C_6H_5(OH)_3$—

$$C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$$

Tannic acid may be itself prepared from gallic acid by heating it with phosphorus oxychloride to a temperature of 130° C For these reasons it is thought that it may consist of two molecules of digallic acid condensed with the elimination of water, thus



There are, however, other tannins which are derived not from pyrogallol but from catechol, $C_6H_4(OH)_2$ These are distinguished from pyrogallol tannins by the following reactions —

Pyrogallol tannins give a blue black colour with a solution of ferric alum, catechol tannins a green black Bromine water gives a precipitate with catechol tannins but none with pyrogallol tannins

CHAPTER VIII.

THE CARBOHYDRATES AND CELLULOSE; HYDRO-CELLULOSE AND OXYCELLULOSE.

CELLULOSE, which is the essential constituent of the cotton hair, belongs to an important group of organic compounds termed carbohydrates. This group includes many of the important natural foodstuffs, such as sugar and starch. All carbohydrates are composed of the elements carbon, hydrogen, and oxygen. The hydrogen and oxygen are always present in some multiple of the formula H_2O.

Thus, glucose, $C_6H_{12}O_6$, might be written $C_6(H_2O)_6$, and cane sugar, $C_{12}H_{22}O_{11}$, $C_{12}(H_2O)_{11}$. As a rule, when a carbohydrate is treated with a powerful dehydrating agent, the hydrogen and oxygen are withdrawn and carbon is left. For such reasons these compounds were termed carbohydrates, but they do not contain water in the sense expressed by the formula H_2O. The carbohydrate group includes many bodies besides cellulose which are of importance in cotton bleaching and finishing. Its members may be divided into the following sub-groups:

1. The sugars.
2. The starches and dextrins.
3. The celluloses.

The Sugars.

Under this name is included a large number of naturally occurring vegetable and animal compounds, which, as a rule, possess a sweet taste and, in many cases, rotate the plane of polarised light. The group includes, also, a number of bodies termed glucosides. These derivatives of sugars are found in many vegetable tissues and under the influence of dilute acids or enzymes are hydrolysed, giving a sugar as one product (Chapter X).

The sugars may be classified as—

1. *Monosaccharoses*, which have the general formula $C_6H_{12}O_6$.
2. *Di saccharoses*, with the composition $C_{12}H_{22}O_{11}$.

The di saccharoses, such as cane sugar, are readily hydrolysed by dilute acids with the formation of two molecules of one or more monosaccharoses:

$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$$

The chief members of these subgroups are—

(*a*) *Monosaccharoses*—glucose (dextrose or grape sugar), fructose (levulose), mannose, galactose.

(*b*) *Di-saccharides*—cane sugar (sucrose), maltose, lactose.

Dextrose, or grape sugar, $C_6H_{12}O_6$, occurs in the juice of ripe grapes. It is found, also, in many other fruits but, usually, accompanied by levulose (fructose).

Both dextrose and levulose are present in honey It is obtained, together with levulose, when cane sugar is heated with a dilute acid, the mixture being known as "invert sugar"—

$$C_{12}H_{22}O_{11}+H_2O=\underset{\text{dextrose}}{C_6H_{12}O_6}+\underset{\text{levulose}}{C_6H_{12}O_6}$$

Dextrose is less soluble than levulose, especially in 70 to 80 per cent alcohol It may be prepared by inverting cane sugar with dilute sulphuric acid at about 50° C., neutralising the acid with barium hydroxide, and, after filtering off the precipitated barium sulphate, concentrating the solution and recrystallising from 80 per cent. alcohol Dextrose is obtained also, when starch is heated for a long time with a dilute solution of a mineral acid (*p. v.*). In this case dextrin, $C_6H_{10}O_5$, is formed as an intermediate product, which is hydrolysed further into dextrose by prolonged boiling with acid—

$$C_6H_{10}O_5+H_2O=C_6H_{12}O_6$$

Commercial glucose, or starch syrup, is generally made in this way After inversion, the solution is neutralised with chalk, the calcium sulphate which is formed filtered off, and the solution concentrated till it crystallises A variable amount of dextrin is always left unhydrolysed Pure dextrose is a colourless substance with a sweet taste It melts at 146° C It is soluble in water, and gives crystals of the composition $C_6H_{12}O_6.H_2O$ It dissolves also in 70 to 80 per cent. alcohol, but is insoluble in stronger spirit, and also in organic solvents such as ether, or petroleum spirit.

Dextrose, in aqueous solution, combines directly with the oxides of calcium, barium, and strontium, giving soluble compounds termed "glucosates," which are decomposed by carbon dioxide with regeneration of the sugar—

$$C_6H_{12}O_6+CaO=C_6H_{12}(CaO)O_6,$$
$$C_6H_{12}(CaO)O_6+CO_2=C_6H_{12}O_6+CaCO_3$$

When heated to a temperature of about 250° C., dextrose is changed into a brown substance termed caramel Traces of acids or alkalis cause this change to take place more readily. When treated with concentrated sulphuric acid, dextrose dissolves and gradually carbonises, though not so quickly as cane sugar. When an aqueous solution of dextrose is digested with yeast, at a temperature of about 20° C, fermentation takes place, with the production of alcohol and carbon dioxide—

$$C_6H_{12}O_6=2C_2H_5OH+2CO_2$$

Other compounds are formed also in small quantities This reaction is caused by an enzyme named "zymase" Yeast contains other ferments also, including invertase and maltase, which are able to change cane sugar and maltose into monosaccharoses.

Dextrose is dextrorotatory, *i e* its aqueous solution rotates the plane of rotation of polarised light to the right The angle through which it is rotated bears a constant relation to the concentration of the solution and the length of the tube in which the solution is contained. By measuring the angle of rotation, by means of a polarimeter, the quantity of dextrose present in the solution can be estimated. Dextrose is a powerful reducing agent It is able to reduce Fehling solution, when boiled with it, giving a precipitate of cuprous oxide, Cu_2O. If the conditions of the experiment are always the same, the weight of cuprous oxide precipitated bears a constant relation to the weight of dextrose present.

By collecting and weighing the cuprous oxide, the amount of dextrose present in the solution used may be calculated. The preparation of Fehling solution is described on p. 92.

The constitution of dextrose is expressed by the formula $CH_2OH(CHOH)_4CHO$, which indicates that it contains both alcohol and aldehyde groups. When dextrose is heated with acetic anhydride and zinc chloride, five acetyl groups (CH_3COO) are introduced—

$$C_6H_{12}O_6+5CH_3COOH=C_6H_7(OOCCH_3)_5O+5H_2O$$

This reaction is similar to that which takes place when ethyl alcohol is treated in the same manner—

$$C_2H_5OH+CH_3COOH=C_2H_5.OOCCH_3+H_2O.$$

In this reaction the hydroxyl is replaced by an acetyl group The same thing is repeated for each alcoholic hydroxyl group present Hence, by heating an organic compound with acetic anhydride and zinc chloride, one can find out if hydroxyl groups are present, and, by analysing the compound formed, determine also their number The zinc chloride acts only as a catalytic agent, *i e* it assists in bringing about the chemical change without being altered itself Since dextrose gives a pentacetate, it must contain five hydroxyl groups, and is a pentahydric alcohol expressed by the formula $C_6H_7O(OH)_5$.

Alcohols may be either—

(1) Primary alcohols, which contain the group CH_2OH, such as ethyl alcohol, $CH_3\,CH_2OH$

(2) Secondary alcohols, which contain the group CHOH, like isopropyl alcohol, $(CH_3)_2CHOH$.

(3) Tertiary alcohols, containing the group C.OH, such as tertiary butyl alcohol, $(CH_3)_3\,COH$

When **primary alcohols,** represented by the general formula $R.CH_2OH$, are oxidised by mild oxidising agents, they are converted into aldehydes of the formula R CHO Thus, with ethyl alcohol—

$$CH_3CH_2OH+O=CH_3CHO+H_2O.$$

When the aldehyde is oxidised, or the alcohol is treated with a strong oxidising agent, an acid is formed Both the aldehyde and the acid always contain the same number of carbon atoms as the original alcohol—

$$CH_3CHO+O\ -CH_3\,COOH$$

These products may be represented by the formulæ (1) RCH_2OH, (2) RCHO, (3) RCOOH. When an aldehyde is reduced with sodium amalgam it is reconverted into a primary alcohol—

$$CH_3CHO+H_2=CH_3CH_2OH.$$

Secondary alcohols behave differently when oxidised, giving, instead of aldehydes, bodies termed *ketones, characterised by the presence of the CO group.* The ketone contains the same number of carbon atoms as the alcohol from which it is produced In the case of isopropyl alcohol the reaction is

$$(CH_3)_2CHOH+O=H_2O+(CH_3)_2CO.$$

The compound $(CH_3)_2CO$ is acetone. Acetone is not oxidised very readily to an

acid, but, when treated with strong oxidising agents, it gives an acid containing fewer carbon atoms than the ketone –

$$(CH_3)_2CO + 4O = CH_3COOH + CO_2 + H_2O$$

When acetone is reduced, it is reconverted into the secondary alcohol—

$$(CH_3)_2CO + H_2 = (CH_3)_2CHOH$$

Tertiary alcohols, when oxidised, give ketones and acids, both of which contain a smaller number of carbon atoms than the alcohol Thus, tertiary butyl alcohol gives both acetone and acetic acid, together with carbon dioxide and other bodies, the molecule being completely broken down

When dextrose is oxidised with bromine water, it gives gluconic acid, which has the formula $CH_2OH(CHOH)_4COOH$ Strong oxidising agents, such as nitric acid, convert it into saccharic acid, $COOH(CHOH)_4COOH$ Both of these acids contain the same number of carbon atoms as the original alcohol When dextrose is reduced with sodium amalgam it gives sorbitol, which is a primary alcohol $C_6H_8(OH)_6$ or $CH_2OH(CHOH)_4CH_2OH$ These facts indicate that dextrose contains primary alcoholic (CH_2OH) and aldehyde (CHO) groups Further evidence is found in the following reactions

1 Both aldehydes and ketones react with phenyl hydrazin, $C_6H_5NHNH_2$, giving bodies termed hydrazones To prepare a hydrazone, a solution of phenyl hydrazin in dilute acetic acid is added to one of the aldehyde in the same solvent, or the two bodies may be simply mixed together The reaction may take place at once, or only on warming, the hydrazone separating as a precipitate or an oil This is filtered off, washed with dilute acetic acid, and recrystallised

The formation of a hydrazone is an important test for the CO group in organic compounds In the case of dextrose the reaction is

$$CH_2OH(CHOH)_4CHO + H_2NNHC_6H_5 = H_2O + CH_2OH(CHOH)_4CHN_2HC_6H_5$$

If excess of phenyl hydrazin be used and the mixture heated another class of product is produced, termed an osazone, aniline being also separated The osazones are less soluble than the hydrazones

The formation of an osazone is represented by the equations

(1) $C_6H_{12}O_6 + 2NH_2NHC_6H_5 = C_6H_{10}O_4(NNHC_6H_5)_2 + 2H_2O + H_2$
(2) $C_6H_5NHNH_2 + 2H = C_6H_5NH_2 + NH_3$

2 Both aldehydes and ketones combine with hydrocyanic acid to form bodies termed cyanohydrins In the case of dextrose this reaction is

$$CH_2OH(CHOH)_4CHO + HCN = CH_2OH(CHOH)_4CH\begin{matrix}OH\\CN\end{matrix}$$

The cyanohydrins, when hydrolysed with a dilute mineral acid, give carboxylic acids and ammonia

$$CH_2OH(CHOH)_4CH\begin{matrix}OH\\CN\end{matrix} + 2H_2O = CH_2OH(CHOH)_4CHOHCOOH + NH_3$$

Levulose, $C_6H_{12}O_6$, occurs together with dextrose, as mentioned above, in honey and many fruits It is also a constituent of invert sugar It is prepared by treating a solution of invert sugar (20 per cent) with slaked lime, keeping the mixture cooled with ice About 6 parts of lime are stirred in little by little to 10 parts of invert sugar dissolved in 50 of water Both dextrose and levulose form glucosates, $C_6H_{12}O_6CaO$ But while the glucosate of dextrose is soluble,

that of levulose is only sparingly soluble in water. The latter is collected on a filter plate, pressed, and washed with a little cold water It is then suspended in water and subjected to a stream of carbon dioxide Calcium carbonate is precipitated and soluble levulose liberated—

$$C_6H_{12}O_6CaO+CO_2=CaCO_3+C_6H_{12}O_6$$

After filtering off the calcium carbonate, the filtrate, when evaporated, gives a syrup consisting of levulose

Artichokes contain a starch called inulin which is soluble in hot water When a solution of inulin is heated with dilute sulphuric acid levulose is produced—

$$(C_6H_{10}O_5)_n+nH_2O=n(C_6H_{12}O_6$$

If the sulphuric acid be precipitated with barium hydroxide, the mixture filtered, and the filtrate evaporated, levulose is obtained Levulose is more soluble in water and alcohol than dextrose It rotates the plane of rotation of polarised light to the left Like dextrose, it is a powerful reducing agent and reduces Fehling solution to cuprous oxide When heated with acetic anhydride and zinc chloride, it gives a pentacetate, $C_6H_7(OOCCH_3)_5O$, and hence must contain five hydroxyl groups It is reduced by sodium amalgam, but gives a mixture of mannitol and sorbitol, both of which have the formula $CH_2OH(CHOH)_4CH_2OH$ In this respect it acts like acetone, $(CH_3)_2CO$ which, when reduced, gives isopropyl alcohol

$$(CH_3)_2CO+2H=(CH_3)_2CHOH$$

When levulose is oxidised with bromine water or nitric acid, tartaric acid, $COOH(CHOH)_2COOH$ and glycollic acid $CH_2OH\,COOH$, are produced Like dextrose, it reacts with phenyl hydrazin giving a hydrazone For these reasons levulose is believed to be a ketone and not an aldehyde like dextrose, and is represented by the formula $CH_2OH(CHOH)_3CO\,CH_2OH$ Levulose is changed into alcohol and carbon dioxide by yeast, but not so readily as dextrose

The Di-saccharoses, $C_{12}H_{22}O_{11}$ The most important member of this group is cane sugar, or sucrose, which occurs in the juices of many plants, notably in the sugar cane and sugar beet It is made from both in the same way The sugar cane is crushed in a hydraulic press to expel the juice Beet is made into a pulp and extracted with water The crude solution thus obtained is neutralised with lime and heated to coagulate dissolved proteins Excess of lime is then precipitated by means of carbon dioxide The solution is then decolorised by treatment with animal charcoal and filtered The filtrate is next evaporated under reduced pressure till it crystallises on cooling The crystals of sucrose are removed centrifuged, and purified by recrystallisation The mother liquid constitutes molasses or treacle Sucrose is a white crystalline substance, readily soluble in water, but only sparingly soluble in alcohol and insoluble in other organic solvents such as ether or benzol. It melts at 160° C , and at about 200° C gives off water and becomes changed into a dark brown substance termed caramel When treated with concentrated sulphuric acid sucrose first dissolves, then blackens, and finally swells up into a mass of carbon Pure charcoal is prepared by powdering and washing this residue

When a solution of sucrose is warmed with a dilute acid it is rapidly hydrolysed into a mixture of dextrose and levulose—

$$C_{12}H_{22}O_{11}+H_2O=C_6H_{12}O_6+C_6H_{12}O_6$$

This mixture, after neutralisation of the acid with barium hydroxide, filtering off the barium sulphate, and concentrating is sold as invert sugar Sucrose is

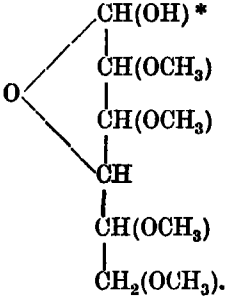
dextrorotatory, but invert sugar is levorotatory. This is because the levorotatory power of levulose is greater than the dextrorotatory power of dextrose. Sucrose, like the monosaccharides, combines with the oxides of calcium or barium, forming soluble sucrosates Calcium sucrosate is used as an adhesive and sometimes for thickening cream. Strontium sucrosate, $C_{12}H_{20}(SrOH)_2O_{11}$, is used in the separation of sucrose from molasses. This is treated with strontium hydroxide The strontium sucrosate is insoluble and is removed by filtration. It is then suspended in water and decomposed by carbon dioxide, the strontium carbonate being removed by filtration from the regenerated soluble sucrose.

Solutions of sucrose do not reduce Fehling solution until they have been inverted by means of acid Neither is sucrose fermented by yeast. But yeast contains an enzyme, termed invertase, which is able to invert cane sugar into dextrose and levulose, which are then changed into alcohol and carbon dioxide by the specific enzyme zymase.

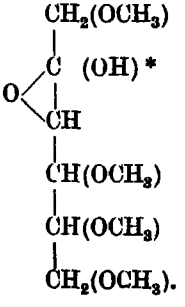
With acetic anhydride, sucrose gives an octa-acetate, $C_{12}H_{14}O_3(OOCCH_3)_8$. Hence it contains eight hydroxyl groups Because of this and, also, on account of the formation of dextrose and levulose when hydrolysed, it is considered that sucrose consists of one molecule of each condensed with the elimination of one molecule of water.

The methods used in the investigation of the structural formula of cane sugar are of considerable interest, because they illustrate the way in which the problem is being attacked in the case of cellulose Sucrose not only gives an octa-acetate but also an octamethyl derivative, $C_{12}H_{14}O_3(OCH_3)_8$

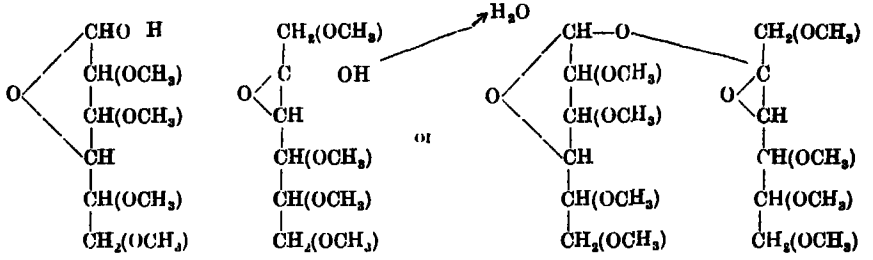
Haworth and Law (*Trans. Chem Soc*, 1916, **109**, 1314) found that, when this octamethyl sucrose was hydrolysed with dilute acid, a tetramethyl glucose was produced, which is believed to have the structural formula



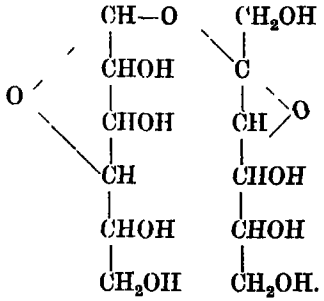
Haworth (*Trans Chem. Soc*, 1918, **113**, 188) isolated also a tetramethyl fructose from the products of hydrolysis of heptamethyl sucrose, $C_{12}H_{15}O_4(OCH_3)_7$ This compound has the following structural formula —



Since it is almost certain that sucrose consists of a dextrose residue attached to a levulose residue, it follows that the union of the two residues must be through the two carbon atoms to which the hydroxyl groups are attached (marked *) in the two methylated products of hydrolysis, one molecule of water being eliminated. Thus the structural formula of octamethyl sucrose by the elimination of water and condensation of the two residues is seen on the diagram.



If the CH_3 groups are replaced by hydrogen, sucrose is obtained. Thus:



This shows that sucrose contains eight hydroxyl groups, and is neither an aldehyde nor a ketone Hence it would not reduce Fehling solution

Maltose, $C_{12}H_{22}O_{11}$, is of some importance in cotton bleaching, since it is formed as one product of the action of diastase, or malt extract, on starch, dextrin being also formed–

$$3C_6H_{10}O_5+H_2O=C_{12}H_{22}O_{11}+\underset{\text{dextrin}}{C_6H_{10}O_5}.$$

Maltose is a solid substance readily soluble in water. It crystallises with one molecule of water. Its solution is dextrorotatory It differs from cane sugar in the following particulars

(1) It reduces Fehling solution (2) It is fermented by yeast, being first hydrolysed to dextrose by an enzyme, maltase, the dextrose being decomposed into alcohol and carbon dioxide by another enzyme, zymase (3) When maltose is hydrolysed by dilute acid it yields dextrose only and no levulose. (4) Like sucrose it gives an octoacetate and reacts with phenyl-hydrazin, forming a hydrazone. It is probably a condensation product of dextrose

Cellobiose, $C_{12}H_{22}O_{11}$, is another important member of this group. It is formed by the action of an enzyme, "cellobiase," on cellulose, and its derivatives, such as acetates, are among the products of acetylosis of cellulose. It bears a relation to cellulose similar to that of maltose to starch, and is of much interest in the study of the constitution of cellulose. It is believed that cellobiose complexes exist in cellulose to the extent of from 33 to 50 per cent.

The Estimation of Sugar.—Sugar can be estimated in two ways—

1. By the polarimeter.
2. By means of Fehling solution.

The latter is, for general purposes, the simplest.

Fehling Solution.—Two solutions are required, viz —

(*a*) 34·63 grammes of pure crystalline copper sulphate dissolved in distilled water and made up to 500 c c

(*b*) 70 grammes of stick sodium hydroxide and 173 grammes of pure Rochelle salt (sodium potassium tartrate) dissolved separately in water, the solutions mixed and made up to 500 c.c

These solutions are kept separate and mixed in exactly equal volumes when required for use Either a volumetric or gravimetric method of analysis may be used

The Volumetric Method.—A burette is filled with a 1 per cent solution of the sugar Ten c c of Fehling solution are placed in a small flask with 40 c c. of water. The flask is placed on a hot plate with the burette just above the neck. The contents of the flask are then boiled gently, and the solution of sugar run in carefully from the burette till the copper sulphate is completely reduced to cuprous oxide. This point is best determined by using Harrison's indicator This is made by boiling 0 05 gramme of starch with a little water, adding 10 grammes of potassium iodide and diluting the solution to 100 c.c. Spots of this indicator are placed on a white tile From time to time a drop of the liquid in the flask is removed by a pointed glass rod and placed on one of the spots, and then one drop of dilute acetic acid is added As long as unreduced copper is present the blue colour of iodide of starch will be developed. As soon as no blue colour is produced the titration is finished and the volume of sugar solution used is read off The quantities of the different sugars exactly reduced by 10 c c. of Fehling solution are—

Dextrose	*0 0500 gramme*
Levulose	0 0500 ,,
Invert sugar	0 0500 ,,
Lactose	0 0678 ,,
Maltose	0·0807 ,,

The Gravimetric Method.—This is more accurate than the volumetric method O Sullivan's process is as follows From 20 to 50 c c of Fehling solution are diluted with an equal volume of distilled water and brought to the boil, or immersed in boiling water. A measured volume of the sugar solution is then run in and boiling continued for two minutes, or the beaker containing the mixture placed in boiling water for fourteen minutes At the end of the heating the liquid must still contain excess of Fehling solution, *i e* it must have a deep blue colour If it is not blue the experiment must be repeated, using less of the sugar solution. The precipitated cuprous oxide is now filtered off on an asbestos mat in a platinum or silica Gooch crucible and well washed with boiling water The mat is then washed successively with alcohol and ether, dried for about half an hour at 100° C , and weighed From the weight of cuprous oxide the equivalent of sugar may be calculated Sometimes the crucible is ignited and the oxide weighed as cupric oxide, CuO. The following table gives the factors for conversion —

	Dextrose	Cane Sugar after Inversion	Lactose.	Maltose
Cu_2O .	0 5042	0 4790	0 6843	0 8132
CuO .	0 4535	0 4308	0 6153	0 7314

The cuprous oxide, after filtration and washing, may be titrated by Knecht's method, as described. Cane sugar must be inverted before it can be estimated by Fehling's method. Fifty c.c. of the solution are placed in a 100 c.c. flask together with 5 c c of hydrochloric acid The mixture is then heated to 70° C for ten minutes, cooled, made alkaline with sodium hydroxide, and diluted to 100 c c. It is then filtered and the invert sugar estimated in the filtrate.

The Polysaccharoses, $(C_6H_{10}O_5)_n$.

This group includes three important kinds of carbohydrates, viz —

1 The starches
2. The dextrins
3. The celluloses.

While the percentage composition of all of these is in agreement with the formula $C_6H_{10}O_5$, yet the molecule is in every case represented by some multiple of this, and is generally written $(C_6H_{10}O_5)_n$ When these carbohydrates are hydrolysed they give one or more monosaccharoses Hence they are believed to consist of molecules of mono- or di-saccharoses, condensed with the elimination of water This is the reason why they are called polysaccharoses.

The chemistry of starch and dextrin will be dealt with under finishing materials in Chapter XXIX , but cellulose must be described here

Cellulose, $(C_6H_{10}O_5)_n$. is the most widely distributed of the natural carbohydrates It forms the chief constituent of all vegetable tissues There are many varieties, which differ chiefly in the readiness with which they are hydrolysed, the products of hydrolysis, and the presence or absence of active ketone (CO) groups. According to Cross and Bevan,[1] they may be classified as follows —

1 Those with maximum resistance to hydrolysis and containing no active CO groups This group includes the cellulose of cotton, flax, ramie, and hemp, which when hydrolysed yield dextrose

2. Cellulose with less resistance to hydrolysis and containing directly active CO groups. These contain more oxygen than the members of group (1), and, owing to the presence of CO groups, they reduce Fehling solution. When hydrolysed with acids they give dextrose and other sugars, and if distilled with hydrochloric acid furfurol, C_4H_3O CHO, is obtained as one product. This aldehyde is prepared by distilling " pentoses " (*i e.* carbohydrates containing five carbon atoms) with acid, while those containing six atoms give none An important member of this group is oxycellulose.

3. Hemi- and pseudo-celluloses. These resemble cellulose in appearance, but are comparatively easily decomposed or hydrolysed. The products of hydrolysis include such bodies as mannose and galactose, $C_6H_{12}O_6$, and pentoses, $C_6H_{10}O_5$.

Tollens (*J.S.C.I.*, 1901, p. 740) divides the celluloses rather differently into

[1] Much of the information given in the following pages has been taken from *Researches on Cellulose*, by Cross and Dorée and Cross and Bevan.

1. Celluloses.
2. Hydrated celluloses, *i.e.* hydro- and hemi-celluloses, which do not reduce Fehling solution but are readily hydrolysed to reducing compounds.
3. Celluloses containing carboxyl groups such as pectins.
4. Celluloses containing both ketone (CO) and carboxyl (COOH) groups, which both reduce Fehling solution and have acid properties.

Both of these classifications include such bodies as hydrocellulose and oxycellulose, which are probably decomposition products of true cellulose. On the other hand, they do not differentiate, simply, between the cellulose of the ordinary textile fibres and that of the more complex vegetable tissues such as wood.

Wolffenstein and Bumcke (*J.S.C.I.*, 1901, p 925) criticise this classification, since the hydrocelluloses (p. 105) and oxycelluloses (p. 109) are generally regarded as hydrated and oxidised derivatives of cellulose. They suggest the following classification: -

1. Celluloses.
2. Hydrated celluloses.
3. Reducing celluloses containing the CO group
4. Reducing celluloses containing carboxyl groups.

Cross and Bevan (*loc cit*) make the following distinctions.—
Cellulose are either (1) simple or (2) compound
Simple celluloses are those of cotton, flax, ramie, etc.
Compound celluloses include—

(*a*) Lignocellulose, the substance of lignified tissues
(*b*) Pectocelluloses and mucocelluloses, which like pectose are readily hydrolysed.
(*c*) Adipocelluloses and cutocelluloses, the substance of cuticular and suberised tissues in which the cellulose is associated with fatty and waxy bodies of high molecular weight

Preparation of Pure Cellulose.—Pure cellulose may be prepared from cotton by the method of Cross and Bevan. This consists of the following operations —

1. Boiling with dilute sodium hydroxide to dissolve proteins, pectins, and oil.
2. Treating the washed residue with chlorine water to oxidise colouring matter.
3. Extraction of the bleached residue with alcohol and ether to remove the last traces of oil and wax.
4. Extracting with dilute acid to remove mineral matter.
5. Repetition of the processes, if necessary

This treatment does not remove the mineral constituents entirely, though it reduces them to very small proportions. In order to obtain ash-free cellulose, treatment with hydrofluoric acid is necessary to remove the last traces of silica.

The Committee of the Division of Cellulose Chemistry to the American Chemical Society have adopted the following process for preparing pure standard cellulose (*J Soc. Dyers and Col.*, 1923, p 302).—

One hundred grammes of Wannamaker's Cleveland raw cotton are carefully cleaned by hand-picking, placed in a nickel gauze container, and boiled four hours in a beaker with 30 grammes of caustic soda, 15 grammes of rosin, and 3000 c.c. of water. The brown alkaline solution is displaced with hot water until the wash water is only slightly alkaline. Most of the rosin is now removed by a further

boiling for fifteen minutes in 3000 c c. of water containing 5 grammes of caustic soda. This solution being displaced by water as before, the cotton is given a third boiling with 3000 c c of water containing 3 grammes of caustic soda. After washing, the cotton is dumped into cold water and allowed to cool. Exposure to air must be avoided during these operations, and means provided for moving the container up and down in the solutions. The cotton is next drained and bleached by immersion in sodium hypochlorite solution (containing 0·1 per cent. available chlorine) at 20° for one hour in diffused light. It is then washed with water for ten minutes on a Buchner funnel and sodium bisulphite solution added drop by drop during the last rinsing, until starch iodide paper shows no reaction. It is now finally rinsed and dried by folding in a cloth surrounded by filter-paper and hand-pressing. In this state it contains negligible traces of fat, which may be extracted with alcohol-benzene mixture if desired.

Properties of Cellulose.—Pure cellulose is a white, odourless, tasteless substance which retains the organised structure of the material from which it was prepared. Its specific gravity is 1·5. It burns freely in air with a luminous smokeless flame. It is hygroscopic, absorbing up to 18 per cent. of moisture when exposed to a damp atmosphere When heated to a temperature of 150° C. it becomes brown in colour. If the heating be continued at this temperature or the temperature be raised, the cellulose decomposes and acid vapours are given off. Prolonged exposure to air or heat for a shorter period at a temperature below 150° C. converts it gradually into a body termed oxycellulose. Cellulose is insoluble in either cold or boiling water, and also in organic solvents. It dissolves in cold concentrated sulphuric and hydrochloric acids, being subsequently hydrolysed to dextrose. It is soluble also in Schweitzer solution, concentrated zinc chloride, or calcium thiocyanate solutions. It adsorbs acids and alkalis to a limited extent, and also certain salts such as copper sulphate. It is not attacked readily by alkalis in the absence of air, though if oxygen is present oxycellulose is produced. Cellulose possibly combines with water, giving a hydrated cellulose, $(C_6H_{10}O_5)_2.H_2O$, which is present in mercerised cotton This is isomeric with another important derivative, hydrocellulose, which is the first product of the hydrolysis of cellulose.

Cellulose is fairly permanent but, under suitable conditions, is attacked by certain enzymes and bacteria. The properties of cellulose are in reality those of cotton. Since these must be described fully, the chief properties of cellulose need only be briefly referred to here. They are—

1. It is readily hydrolysed by acids, with the formation of dextrose.
2. Is fairly resistant to alkaline hydrolysis.
3. Forms more or less definite adsorption compounds with sodium or potassium hydroxide.
4. Is converted by oxidising agents into derivatives containing ketone (CO) and carboxyl (COOH) groups.
5. Forms ethereal salts with many organic acids and nitrocelluloses with nitric acid.
6. Its adsorption compounds with sodium oxide form xanthates or thiocarbonates when treated with carbon bisulphide.

The Constitution of Cellulose.—The percentage composition of all kinds of cellulose is represented by the formula $C_6H_{10}O_5$, but it is certain that some multiple of this must be taken to represent the molecule. The exact multiple is a matter of considerable uncertainty, and, hence, the formula is written generally as $(C_6H_{10}O_5)_n$.

The constitution of cellulose is still unknown, although it has been the subject of much investigation. Its importance is equalled only by its difficulty, and the constitution of cellulose has become almost a special branch of organic chemistry. The molecular weight cannot be determined, since no known solvent dissolves cellulose without changing its chemical properties or physical condition. Owing to its colloidal nature, and consequent complexity, the products of its decomposition are not easy to separate and determine quantitatively, and this must be done before any attempt can be made to prepare a chemical compound by synthesis

The chief facts connected with the chemistry of cellulose are—

1. It contains hydroxyl groups Four are possibly present in each $C_6H_{10}O_5$ unit, since, when cellulose is heated with acetic anhydride and zinc chloride, a tetra-acetate, $C_6H_6O(OOCCH_3)_4$, is produced This led Cross and Bevan to propose, originally, the formula $C_6H_6O(OH)_4$ It may be noted, however, that Perkin and Green (*J S C.I.*, 1906, p. 652) could not prepare a cellulose acetate containing more than three acetyl groups. These hydroxyl groups must be alcoholic in nature, and since, when oxidised, both carboxyl and ketone groups are introduced, both primary and secondary alcoholic groupings must be present. That is, the molecule contains both CH_2OH and CHOH groups

2 Cellulose itself does not reduce Fehling solution, nor form hydrazones when treated with phenyl-hydrazin Nor does it exhibit any of the properties of an acid Hence neither carbonyl nor carboxyl groups can be present

3 When cellulose is completely hydrolysed by dilute acids it gives dextrose, $C_6H_{12}O_6$, the constitution of which is known, while partial hydrolysis produces bodies having reducing properties, *i e* containing carbonyl groups

4 Under the influence of acetic anhydride an octa-acetate of cellobiose, $C_{12}H_{22}O_{11}$, is produced, while lævoglucosan is obtained by distillation under reduced pressure.

5. Since derivatives of benzene can be obtained from cellulose, it is assumed that it is built up on the type of a closed ring as opposed to an open chain Further, the group $CO—CH_2$ must be present, because when cellulose is fused with alkalis, hydrogen, and carbonic, acetic and oxalic acids are formed.

The following is taken from *Researches on Cellulose* (Cross and Dorée), p. 65.—

"The solution of the problem of cellulose constitution has taken its place as a definite objective of the systematic science, and since the researches towards this end are based upon rigorous quantitative method, the results are important accumulations of data which must be accepted as exact There are several methods, or lines of attack, with the common aim of resolving the cellulose into bioses, or monoses, or their ester-ether derivatives, quantitatively estimating these, and from the yields and constitution (configuration) deducing an integral constitutional formula for the parent complex.

"The characteristic features of these several methods are as follows, cotton cellulose being generally adopted as the typical cellulose and parent substance —

"1. Solution of the cellulose in 'mineral acids,' H_2SO_4 . . . $H_2SO_4.2\frac{1}{2}H_2O$, HCl, Aq (41 to 42 per cent. HCl), dilution with water, and boiling to complete the hydrolysis.

"2. Solution in acetic anhydride, in presence of sulphuric acid: acetolysis to cellobiose-octacetate.

"3. Conversion to methyl- and ethyl-ethers by interaction of alkali-cellulose and sulphuric esters and resolution of these.

"4. Distillation under reduced pressure yielding lævoglucosan.

"The results obtained under these several sections are by no means uniform or uniformly interpreted; this conflict of results, or interpretation, is in itself a progressive criticism, elucidating the terms of ultimate common agreement. Outside any question of interpretation the following very definite stages of progress have been achieved –

"(*a*) The recognition of cellobiose as the cellulose sugar; the proof of its constitution and its relationship to maltose.

"(*b*) The recognition of lævoglucosan as a definite cleavage product. a carbohydrate of C_6 dimensions produced in large proportion to the original (50 per cent), and by a process which, although technically described as destructive, is not severe as regards constitutional change. Constitution probably settled.

"(*c*) Preparation of methyl derivatives and their resolution, particularly, to a crystalline trimethyl glucose of known constitution."

The Hydrolysis of Cellulose.—If dextrose be the final product of the hydrolysis of cellulose, it would indicate that cellulose may be formed by the condensation of dextrose with the elimination of water. Thus·

$$2C_6H_{12}O_6-H_2O=C_6H_{10}O_5.$$

But if this be so the theoretical quantity of dextrose should be obtained when cellulose is hydrolysed. According to the equation

$$C_6H_{10}O_5=H_2O+C_6H_{12}O_6,$$

100 parts of cellulose yield 111 parts of dextrose.

Ost and Wilkening (*Chem. Zeit*, 1910, **34**, 461, *J S C I*, 1910, p 688) converted cellulose into dextrose almost quantitatively by the following process: Five grammes of cellulose were dissolved in 50 c c of 72 per cent. sulphuric acid, and after standing three hours, the solution was diluted to a content of 3 per cent of sulphuric acid and 0·25 per cent. of cellulose products, and finally digested in an autoclave for two hours at 110° C Estimation of the dextrose formed gave 100·4 per cent on the cellulose taken Organic acids which formed barium salts were also present to the extent of 4·3 per cent (calculated as H_2SO_4) on the cellulose. The specific rotatory power of these was α_D 44·8, and 1 gramme of the solid gave 1·15 grammes of dextrosazone

Monier-Williams (*J. Chem Soc*, 1921, **119**, 803), who used sulphuric acid as the hydrolysing agent, obtained a yield of crystalline dextrose amounting to 90·67 per cent. of the theoretical quantity. It should be noted that it is rarely possible to separate and weigh the whole of the products of hydrolysis, and a total yield of 90 per cent, especially as no other body was identified, may be regarded as satisfactory and to indicate that dextrose is the only product. But Wohl and Blumrich (*J.S C I*, 1921, 158A), using hydrochloric acid as the hydrolysing agent, concluded that two bodies are produced, namely, dextrose and a higher carbohydrate, the latter being capable of being hydrolysed further. Cunningham (*J.S.C I.*, 1918, 236A) also concluded that no quantitative resolution of cellulose into dextrose has been obtained.

Irvine and Soutar (*J. Chem. Soc.*, 1920, **117**, 1489) state that a normal

cotton cellulose is represented by the formula $(C_6H_{10}O_5)_n$, and is probably a polyglucose anhydride. The complex may consist of simple $C_6H_{10}O_5$ units, derived from hexose by molecular loss of water, polymerised in unknown numbers, but, on the other hand, n molecules of a hexose may be connected together directly, through the elimination of n molecules of water, or, where n is a large factor, $(n-1)$ molecules. In either case the first point to be settled is to ascertain, beyond doubt, if glucose is actually the hexose formed by the hydrolysis of cellulose, and, if so, to determine exactly the amount of sugar thus produced. The inquiry becomes more definite if it can be shown that, within the limits of reasonable experimental error, cellulose can be converted into glucose in terms of the equation

$$(C_6H_{10}O_5)_n + nH_2O = nC_6H_{12}O_6.$$
$$100 \longrightarrow 111{\cdot}11.$$

The claims which have been made from time to time that practically quantitative yields of glucose have been obtained from cellulose are criticised adversely "Up to the present time, in no research on the hydrolysis of cellulose, where a yield of glucose, even approximately to the theoretical amount, has been claimed, have the results been based on the quantity of the sugar or of a characteristic derivative *actually isolated.*"

But in the work described the weight of hexose was ascertained from that of the crystalline compounds obtained in a state of purity and in well-defined stereochemical forms Adopting this standard, Irvine and Soutar proved that the minimum yield of glucose from cellulose is 85 per cent of the theoretical quantity The method used was as follows Cellulose was treated with a large excess of acetic anhydride and sulphuric acid When the fibrous structure had disappeared the product was poured into water and the precipitated solid acetate separated The filtrate then contained the lower acetylated glucoses together with acetosulphates and other soluble degradation products, whilst the insoluble residue consisted of polysaccharide acetates The latter were heated in an autoclave at 100° C with methyl alcohol containing 0 5 per cent of dry hydrochloric acid gas. This first removed the acetyl groups which were converted into methyl acetate Then simultaneous hydrolysis and condensation with the solvent ensued. The main product of the reaction consisted of a crystalline methyl glucoside, but about 25 per cent of the material remained, and was unaffected on repeating the treatment with methyl alcohol and hydrochloric acid. This amorphous residue was hydrolysed with dilute aqueous hydrochloric acid and the product of hydrolysis again treated with the acid alcohol In this way the total yield of methyl glucoside from the fraction insoluble in water was obtained Pure crystalline glucose was easily prepared from this compound It is uncommon in the sugar group to obtain crystalline derivatives in yields which exceed 80 per cent Hence a yield of 85 per cent. affords strong evidence that cotton cellulose is composed essentially of glucose residues condensed together The methyl glucoside obtained was isolated from three groups of acetolysis products, viz —

A. Soluble in water.
B. Insoluble in water and hydrolysed by methyl alcohol.
C. Insoluble in water and resistant to acid methyl alcohol

The quantities of methyl glucoside obtained show that the cellulose molecule may be dissected into three portions, A, B, and C. The approximate ratio in which these are present are—

Cellulose 100 Parts	Methyl Glucoside	Equivalent to Dextrose	$C_6H_{10}O_5$
A gave	9 5817	8 9	8 0
B gave	52 3372	48 6	43 7
C gave	39 9068	37 0	33 3
		94 5	85 0

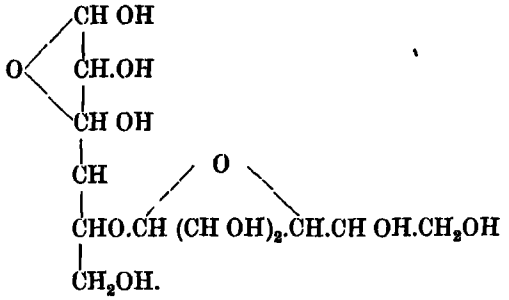
That portion of the cellulose molecule which is most resistant to hydrolysis agrees closely with the maximum yield of cellobiose octa-acetate obtained from cellulose, and this di-saccharide represents apparently the most resistant portion of the cellulose molecule

Cellobiose.—*It has been mentioned above that cellobiose is a di-saccharide* isomeric with maltose, and that it is obtained as an octa-acetate when cellulose is treated with acetic anhydride under suitable conditions, and also that the action of the enzyme cellobiose produces small quantities of this sugar when it acts on cellulose Cellulose is rather resistant to chemical changes, and hence cellobiose, which is *much more reactive, forms a convenient starting-point* in researches in connection with the constitution of cellulose.

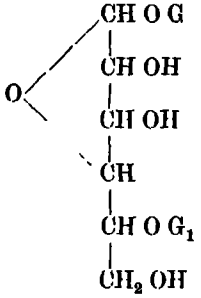
As stated above, when cellulose is decomposed by acetic acid, acetates of cellobiose are produced Ost (*J S C.I*, 1913, p. 784) found that, when cellulose is acetylated by a mixture containing sulphuric acid and a catalyst, the solution loses its viscosity on standing, and a range of dextrin acetates is produced terminating in cellobiose octa acetate and dextrose penta-acetate The best *results are obtained with a mixture of acetic anhydride and glacial acetic acid* containing 10 grammes of sulphuric acid per 100 c c Cellulose was digested with about eleven times its weight of such a mixture at 18° to 20° C for from four to six months From the reaction products, a certain amount of cellobiose acetate crystallises out, the liquid is poured into water, and the dried precipitate is extracted with ether The insoluble matter contains cellobiose acetate and acetates of intermediate dextrins The former separates on crystallisation from 70 per cent alcohol, *while the dextrin acetates are precipitated from the mother* liquid by water The ethereal extract of the precipitate, and of the portion of the reaction product soluble in water, contains the dextrose acetate. A portion of this crystallises out as penta-acetate, and further quantities may be prepared by subsequent acetylation of the residual syrups Of crystallisable products, cellobiose and dextrose acetates, 60 6 per cent of the theoretical quantity were obtained, while that recovered from the residues brought the percentage up to more than 92 The residual syrups were *identical with those obtained from dextrose*, and Ost concluded that the cellulose molecule is composed entirely of dextrose residues.

In the results of Irvine and Soutar quoted above, a total deficiency of 15 per cent was recorded They think that it is conceivable that this may be accounted for by the presence of a nucleus in the cellulose molecule which is resolved into a ketone group on hydrolysis. The yield of cellobiose acetate never exceeded 60 per cent. equivalent to 31·9 per cent. of glucose. It would appear, therefore, that *at least one-third of the cellulose molecule contains the* linkage characteristic of cellobiose, which contains eight hydroxyl groups, one of which has reducing properties and is therefore terminal. It follows that one of the remaining hydroxyl groups of the reducing component must be attached to the reducing group of the second glucose residue. The position of this linkage

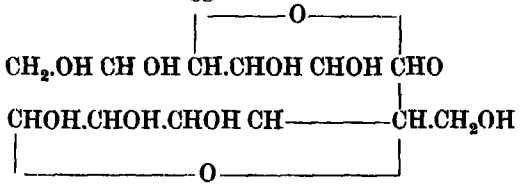
may be fixed from (among other factors) the constitution assigned to trimethyl glucose, and the following formula may be deduced for cellobiose —



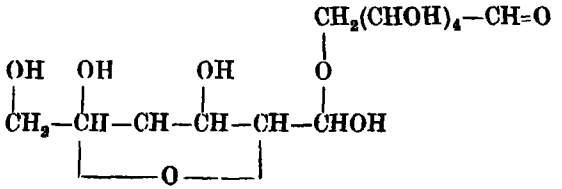
The expanded structure below, in which G and G_1 represent glucose residues, can thus be deduced for a fragment of the cellulose complex.



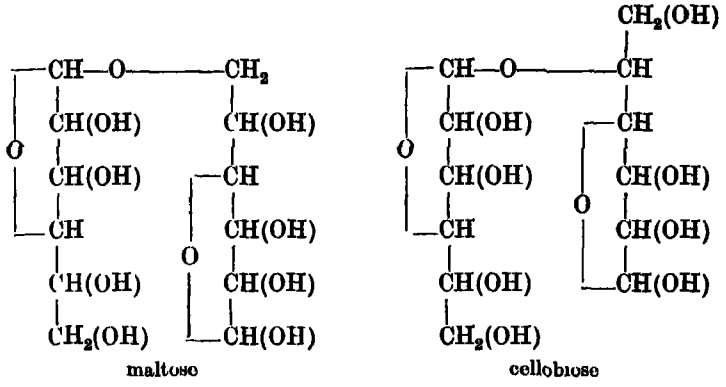
Other investigators have arrived at different conclusions with regard to the constitution of cellobiose Dorr (*J. Soc Dyers and Col*, 1924, p 16) states that when cellulose is acetolysed with acetic anhydride and a little sulphuric acid, cellodextrins are first produced and then cellobiose. The latter is a well-defined crystalline compound with a specific rotatory power of $\alpha_D = +34\ 6$ and a constant reducing power, and forming an ozazone. Cellobiosé can be oxidised to a monobasic acid, cellobionic acid, and its empyrical composition is identical with that of maltose, from which it differs in its reducing power, the melting-point of its ozazone, and in being scarcely fermentable. An isomeric cellobiose has been isolated by Ost. The formula suggested for cellobiose is



Von Euler (*J S C I*, 1921, 764A) suggested another constitution for cellobiose, viz —

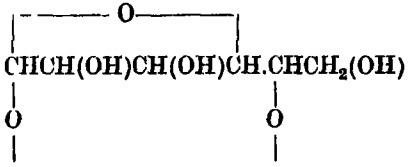


Haworth and Hirst (*J.S.C.I.*, 1921, 234A) and Haworth and Leitch (*J.S.C.I.*, 1919, p. 691) have suggested the following formulæ for cellobiose and maltose:—



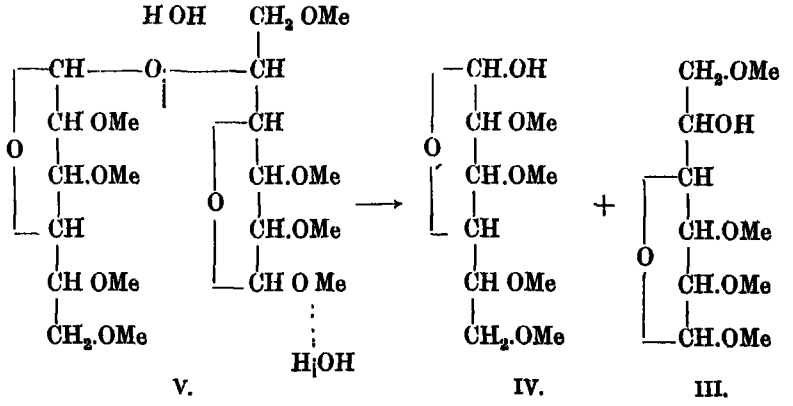
maltose cellobiose

Haworth and Hirst think there is evidence of a structural linking for the part of the glucose constituent of the type



which is linked with other residues through both the reducing and hydroxyl groups attached to the fifth carbon atom from the reducing end of the hexose chain

The method used by Haworth and Hirst was the study of the products of the methylation of cellobiose. They obtained a heptamethyl methylcellobioside (melting-point 76° to 78° C.) of the formula (V)—

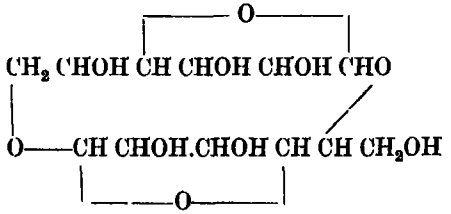


V. IV. III.

Of the eight methyl groups in this compound protecting the hydrolysis, one is easily eliminated, namely, that protecting the very labile reducing group of the biose. On the cleavage of the di-saccharide grouping, two or more hydroxy

groups are released, namely, the one participating in the union of the two hexose residues. When this was done in the laboratory, the products isolated were the butylene oxide forms (*a*) of trimethyl (formula III), and (*b*) of tetramethyl glucose (formula IV), the former being identical with that previously isolated from cellulose

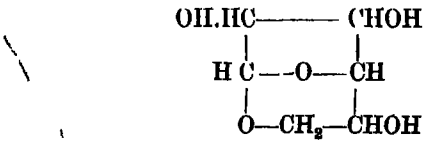
Hess (*Ber*, 1921, **54**, 3232) prepared an acetylethyl derivative of cellulose by acetolysis of highly ethylated cellulose Upon saponification with sodium methylate he obtained an ethyl degradation product with no reducing power and incapable of swelling It was soluble in organic solvents, and its molecular weight was found to be from 800 to 900 This body associates in concentrated solutions It contains, at most, four glucose residues, and is either a fourfold associated ethylglucose anhydride or a twofold associated ethylcellobiose anhydride. By treating cellobiose with acetyl chloride, Hess (*Ber.*, 1921, **54**, 2867; *J Soc Dyers and Col*, 1924, p 18) obtained cellubiose anhydride—



which is very similar to cellulose It is insoluble in water, but dissolves in dilute caustic soda and cuprammonium solution It can be fermented by specific bacteria Hess considers it to be the basis of cellulose

A yield of only 37 to 43 per cent of cellobiose can be obtained, but Karrer considers that at least 50 per cent must be already present in cellulose He regards starch as being built up from tetra-amylose and, analogously, cellulose from dicellobiose anhydride, since the heats of combustion of cellulose and starch are the same The cellulose molecule is, therefore, really small, $(C_{12}H_{20}O_{10})_2$ These dicellobiose anhydride molecules are symmetrically bound together, to a high degree, by crystal-valencies, which are almost as strong as the polymerisation valencies and the valencies within the cellobiose anhydride molecule, so that it will be difficult to find reagents which will break down the crystal without destroying the cellulose molecule or the cellobiose anhydride complex. The latter are supposed to be arranged at the lattice points of the crystal system, and this hypothesis is supported by the X-ray investigations of Herzog and Janke (*Ber*, 1920, **53**, 2162).

Lævoglucosan, $C_6H_{10}O_5$, was obtained by Pictet and Sarasin (*J.S C.I*, 1918, 49A) as one product of the dry distillation of cellulose under reduced pressure. Its structure is represented by the formula



The same compound was prepared also from starch and dextrin. These authors suggested that lævoglucosan may be a product of depolymerisation of cellulose

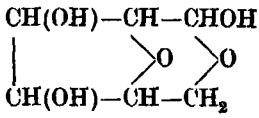
or, conversely, that the cellulose molecule may consist of polymerised lævoglucosan.

Formulæ suggested for Cellulose.—Many theories have been put forward to explain the constitution of cellulose, some of which are very simple and others as complex.

Comparatively recently Hess, Weltzien, and Messmer (*Annalen*, 1924, **435**, 1–144) (from *J Text. Inst.*, 1925, 44A) have shown that in cuprammonium-cellulose solutions there is a copper cellulose complex in which copper is present both in an optically active complex anion and also in amine cations As the result of detached experimental work the above authors conclude that, "in cuprammonium solutions containing 5 28 molecules of copper per 100 litres, cellulose up to 15 molecules and 25 molecules of sodium hydroxide, the cellulose behaves as though it were $C_6H_{10}O_5$."

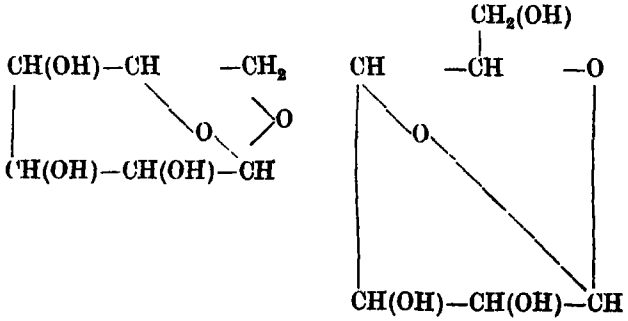
The further conclusion is drawn, that cellulose consists of an association or aggregate of $C_6H_{10}O_5$ units, that is, it is neither a polymeride (in which the whole would have different physical and chemical properties from the units) nor a condensation product in the chemical sense. In other words, the authors support Green's formula for cellulose and, in the light of Irvine's work, assume an amphoteric molecule, with an oxygen bridge, carrying a positive and a negative charge, the units being held together by residual affinity. On the evidence of X-rays each cellulose crystallite consists of an aggregate of four units, and the different properties of different celluloses are explained on the assumption that in normal cellulose these crystallites are in the most compact order, whereas their arrangement is more and more haphazard in forms of greater solubility and lower viscosity.

It is interesting to note that Green (*J.S.C.I.*, 1904, p 382) did not consider that there were sufficient reasons for this assumption, and that cellulose was more probably represented by the formula $C_6H_{10}O_5$ than by some multiple of it. He proposed the following formula.—



This represents cellulose as an inner anhydride of glucose, $CH_2OH(CHOH)_4CHO$.

Somewhat similar simple formulæ were suggested also by Vignon and Hibbert. These were—

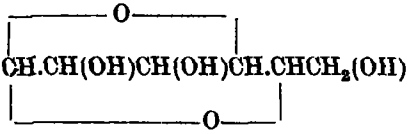


Vignon Hibbert

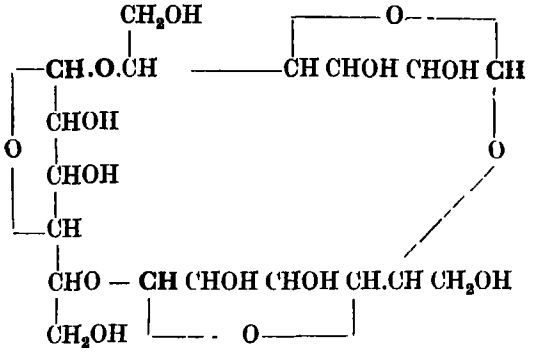
Irvine and Hirst (*J.S.C.I.*, 1923, 710A) have recently proposed a further

formula based upon a study of trimethyl-cellulose, $C_6H_7O_2(OCH_3)_3$, the hydrolysis of this body to a methylated glucose, and the condensation of this with methyl alcohol and hydrochloric acid gas. Trimethyl-cellulose when hydrolysed gave only one sugar, namely, 2 . 3 . 6 trimethyl-glucose.

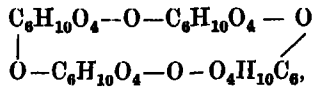
The simplest formula possible is



But this would not yield a cellobiose. The above formula is a 1-5-anhydro-glucose, but the simplest structure which would be in conformity with the facts of their experiments would be a dianhydroglucose of the same unit structure. The authors consider that a grouping which would give a yield of 70 per cent of cellobiose is necessary, and suggest the following formula as meeting these requirements, the letters in black type indicating potential reducing groups



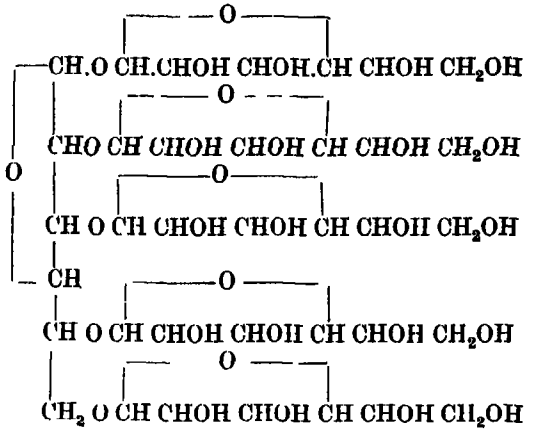
Herzog and Janke (*Ber*, 1920, **53**, 2162) established the fact that cellulose is krypto-crystalline, and, in fact, crystographically not lower than monoclinic and probably rhombic. They consider that, during the growth of the plant, the constituents of the cellulose are being placed in position Herzog and Polany have used these results to determine the constitution of cellulose Four glucose residues are regularly repeated, and are to be regarded as lattice points, and they consider cellobiose to be the fundamental basis of the crystal Cellulose is built up either from a chain of four glucose residues or a ring chain,



or from internal anhydrides of cellobiose. The latter agrees closely with Karrer's results. Hence cellulose is considered to be a complex alcohol built up from cellobiose anhydride, though this does not account for the formation of isosaccharic acid from oxycellulose (Tollens) nor of cellobiosobiose (Ost)

The view of Pictet and Sarasin in connection with lævoglucosan has been mentioned.

Hess (*J. Soc. Dyers and Col.*, 1924, p. 18) suggested that cellulose is a pentaglucosidylglucose with the formula



This is regarded as representing the molecule of a degradation product of cellulose, hydrated or swollen cellulose, which may be termed "celluxose" The celluxose molecules, by exercising residual affinities, arrange themselves into the great cellulose molecule

Hydrocellulose is one of the first products of the hydrolysis of cotton by means of acids. It was thought, originally, that it was represented by the formula $C_{12}H_{22}O_{11}$ or $(C_6H_{10}O_5)_2H_2O$, and produced in accordance with the equation

$$2C_6H_{10}O_5+H_2O=C_{12}H_{22}O_{11}.$$

Later work showed that when cotton is boiled with dilute hydrochloric or sulphuric acid, hydrocellulose is produced together with a sugar of the same reducing power and optical activity as dextrose Prolonged hydrolysis converts the former substance into a dextrose—

$$3C_6H_{10}O_5+2H_2O=C_{12}H_{22}O_{11}+C_6H_{12}O_6,$$
$$C_{12}H_{22}O_{11}+H_2O-2C_6H_{12}O_6$$

Stern (*J S.C.I*, 1904, p. 265) showed that when dilute acids act upon cellulose, so as to produce hydrocellulose, there is no gain in weight, as would be required by the usually accepted formula $C_{12}H_{22}O_{11}$, but an actual loss At the same time a small amount of soluble matter, probably glucose, is formed The elementary composition of the residual powder is identical with that of cellulose, and he concluded, therefore, that under these conditions a hydrated cellulose is not formed. Schwalbe considered that hydrocellulose is represented by the formula $(C_6H_{10}O_5)_6H_2O$, while Stern suggested $(C_6H_{10}O_5)_7H_2O$.

Closely related to hydrocellulose is the product formed by the action of alkalis, also represented by the empyrical formula $(C_6H_{10}O_5)_2H_2O$. This body is produced during the process of mercerisation (Chapter IX). It differs from hydrocellulose, prepared by acid hydrolysis, in certain important respects. Hydrocellulose produced by acids causes destruction of the cotton fibre and consequently tendering. That obtained by the action of alkalis, on the contrary, increases the tensile strength very greatly. Cotton which has been tendered by the action of acids

can be strengthened by treatment with alkalis. Schwalbe considers that this form of hydrocellulose is represented by the formula $(C_6H_{10}O_5)_2H_2O$.

Cross and Bevan and others also hold that hydrocellulose is a definite chemical compound, relying chiefly on its different action with chemical reagents and solvents.

Hess and Wittelsbach (*J.S.C.I.*, 1920, 512A) suggest that the molecule of hydrocellulose, for which the name celluxose is proposed, consists of a dextrose or a cellobiose molecule in which the hydroxyl groups are etherified by dextrose or cellobiose residues. The formula

$$\begin{array}{l} CH(OX)\ CH(OX).CH(OX)\ CH\ CH(OX).CH_2(OX) \\ \quad\quad\quad\

cellulose was similar to the untreated hydrocellulose, and was not cellulose since the viscosity of its solution in cuprammonium solution (after twelve hours at 19° C.) was equal to the viscosity of a similar solution of the original hydrocellulose, but approximately only one-half of a similar solution of the purified cellulose Moreover, the residue, after digestion with lime water, gave on acetylation, under various conditions, a cellulose acetate with a solubility in acetone similar to that of the acetate of the original hydrocellulose, but much greater than that of the corresponding acetate made from the purified cellulose. Pringsheim (*Cellulosechemie*, 1921, **2**, 57) agrees with Ost and Bretschneider that hydrocelluloses are definite substances, while J. E Minor (*J S C.I*, 1921, 175A) argues that the first stage in the decomposition of cellulose is the formation of mucilaginous soluble dextrins which are, at once, adsorbed by the cellulose yielding the aggregate termed hydrocellulose The whole question is rendered difficult of solution by the fact that it is almost impossible to prepare hydrocellulose without at the same time obtaining some oxycellulose, while some of the properties ascribed to it may be those of the adsorption compounds of cellulose with the acid used to hydrolyse it

The Preparation of Hydrocellulose.—Hydrocellulose is produced when cellulose or cotton is treated with cold concentrated mineral acids. Further details of this action will be given later It is obtained also when cellulose is heated with a dilute solution of an acid, or even soaked for a long time in a cold solution The rate of the transformation depends upon (1) the hydrogen-ion concentration of the acid; (2) the concentration of the solution used, (3) the temperature of the reaction; (4) the presence or absence of air.

Thus, if cotton be soaked in a cold dilute solution of sulphuric acid, the action is extremely slow. But if after impregnation it be squeezed and exposed to the air the hydrolysis becomes more rapid If cotton be boiled with dilute sulphuric acid hydrocellulose is produced fairly rapidly, while at temperatures above 100° C the action is very greatly accelerated At a pressure of about 2 atmospheres mere traces of sulphuric or hydrochloric acid cause almost complete hydrolysis, and when the cotton is dried it breaks down into a powdery mass In the carbonisation of wool, the material is impregnated with a 5 per cent. solution of sulphuric acid, dried at a low temperature, and then heated to a temperature of from 70° to 100° C for two hours. This converts the vegetable fragments into hydrocellulose which can be either washed or shaken out of the wool As little as one part of hydrochloric acid (or sulphuric acid) in 10,000 parts of cotton will, if dried in, gradually transform it into hydrocellulose.

For experimental purposes the following methods are suitable Girard's (*J S.C.I*, 1922, 458A) method consists of soaking viscose or cotton in a 3 per cent solution of hydrochloric acid, pressing the solution out, till that retained is equal in weight to the weight of cotton, drying by exposure to air, and then heating in a closed vessel at 70° C for four hours In Lederer's process, air-dry viscose cellulose is heated with 98 per cent. acetic acid containing 0·25 per cent. of hydrochloric acid, the acetic acid acting simply as a distributing agent.

Knoevenagel and Busch (*ibid.*) recommend the following as the most convenient method. The air-dry cellulose or viscose is treated with dry hydrogen chloride in a closed evacuated vessel at ordinary temperature. The percentage of acid absorbed corresponds with the amount of moisture in the cellulose, and, by regulating the degree of humidity and the time and temperature of the reaction, the conversion can be so controlled that a product completely soluble in 8 per cent. sodium-hydroxide solution is obtained which is precipitated, substantially without loss, on acidifying the solution. With viscose cellulose of normal

humidity (11 per cent.), the reaction at ordinary temperatures requires about twelve hours, with lower humidity a longer time is necessary, and with excessive moisture the reaction may proceed too far, giving low yields. The conversion into alkali-soluble hydrocellulose does not take place if the cellulose be dried completely. Only cellulose modified or hydrated in certain ways is capable of forming the alkali-soluble product. Viscose cellulose yields it most readily. With cellulose regenerated by the saponification of cellulose acetate, the solubility of the product is only one-tenth of that of hydrocellulose produced from viscose. Gaseous hydrofluoric or hydrobromic acids act in the same way as hydrogen chloride.

Heuser and Eisenring (*J.S.C.I.*, 1923, 649A) treated viscose cellulose, containing from 8·3 to 11·8 per cent of moisture, by the method of Knoevenagel and Busch, and obtained a product soluble in 8 per cent. sodium-hydroxide solution and reprecipitated almost quantitatively by alcohol. With larger quantities of water the hydrolysis was more profound, and the product gave, when partially hydrolysed, increasing quantities of dextrose Hydrocellulose from viscose, completely soluble in caustic alkali, gave when completely hydrolysed over 90 per cent of fermentable dextrose. The substance precipitated by alcohol from the solution of viscose hydrocellulose in strong caustic alkali, and washed to exhaustion with absolute alcohol, has a composition corresponding to the formula $C_{12}H_{22}O_{11}$ 2NaOH. They prepared, also, a similar alkali-soluble hydrocellulose by heating viscose cellulose in a sealed tube with oxalic acid (8 to 16 per cent.) at 100° C. for from one and a half to twelve hours.

Naturally, acid salts, and salts which dissociate in aqueous solution, act in a similar manner to acids, though less rapidly on account of their different hydrogen-ion concentrations

The action of weak acids such as organic acids is also determined by their hydrogen-ion concentration, and also by their volatility Oxalic acid which is not volatilised tenders cotton readily when dried into it or heated. Acetic and formic acids have much less effect

Jentgen (*J. Text Inst*, 1923, T. 70) distributes the acid or salt of the acid with a weak base through the cellulose by means of a non-dissociating solvent such as glacial acetic acid, ether, amyl acetate, formic acid, or glycerol He suggested that, in the production of hydrocellulose, the acid enters into association with the cellulose by adsorption, and that hydrolysis proceeds by the action of finely divided water on the adsorption compound, the acid acting as a contact agent. If moisture be rigorously excluded no hydrolysis takes place, and the cellulose can be recovered quantitatively by washing the adsorption compound. This, however, appears to be simply a restatement of the fact that acids can only become ionised in the presence of water

Hydrocellulose can be prepared also by the prolonged heating of cellulose with steam at a pressure of from three to four atmospheres.

The Properties of Hydrocellulose.—Hydrocellulose is more readily affected by heat than cellulose. It begins to become yellow at about 130° C., while cotton is not changed till 150° C is reached. It dissolves more readily in solvents such as Schweitzer solution than ordinary cellulose. It has a greater affinity for basic dyestuffs, such as methylene blue, than ordinary cellulose, and a decreased affinity for diamine sky-blue, a direct dyestuff. This decreased affinity is not affected by boiling with sodium hydroxide. This forms the basic of Knecht's test, described later. Hydrocellulose reduces Fehling solution. This reducing action is measured quantitatively by means of Schwalbe's copper value (described under oxycellulose). The copper value of cellulose is not more than 0·2. For

hydrocellulose it varies from about 3·5 to 10·5 according to the degree of hydrolysis.

The alkali-soluble form, described above, is said to have a copper value of 14 which is practically the same as that of oxycellulose. But according to the experiments of Hauser and Herzfeld, quoted above, this is only due to the formation of dextrose. When hydrocellulose is boiled with milk of lime calcium isosaccharate is produced together with other products. Briggs (*Chem. Zeit.*, 1910, **34**, 455) found that hydrocellulose adsorbs more alkali from solution than cellulose, and adsorbs more from an alcoholic than from an aqueous solution.

Hydrocellulose is also transformed into esters more readily than cellulose. The alkali-soluble form was found by Knoevenagel and Busch to be exceptionally amenable to benzoylation and acetylation It formed a tribenzoate completely soluble in chloroform. It gives certain colour reactions, most of which are common to oxycellulose and will be described later

Oxycellulose, $C_{18}H_{26}O_{16}$, is formed when cellulose is acted upon by an oxidising agent, or by acids or alkalis in presence of air, with or without the assistance of certain catalytic agents such as the oxides of iron or copper. Nitric acid, permanganates, bichromates, peroxides, persulphates, hypochlorites, chlorine, and other similar oxidising agents all have the power, under suitable conditions, of changing cotton or cellulose into oxycellulose. In the bleaching of cotton, by means of bleaching-powder solution, the residual colouring matters are attacked first and protect the cellulose from oxidation. If, however, too great an excess of chlorine be present or other unsuitable conditions obtain, the reaction proceeds further and the cotton becomes " overbleached," *i e* partly converted into oxycellulose.

Preparation of Oxycellulose.—Cross and Bevan found that nitric acid of from 1·1 to 1 3 specific gravity attacks cellulose, at first slowly, and afterwards more rapidly, but tending to reach a limit at which the action again becomes slow This action is accompanied by the formation of oxycellulose, the limit corresponding with a body of the composition $C_{18}H_{26}O_{16}$ This is a white flocculent substance which amounts to 30 per cent of the cotton treated, the remainder being oxidised to simpler compounds such as oxalic and carbonic acid. It combines with water, forming a gelatinous hydrate, and dissolves in a mixture of nitric and sulphuric acids. When the solution is poured into cold water a nitrate separates out having the composition $C_{18}H_{23}O_{13}(NO_3)_3$

Nastukoff (*J S C I*, 1902, p. 63) obtained a much higher yield amounting to 90 per cent of the original cellulose by the following process. A quantity of nitric acid, of 1 3 specific gravity, is taken equal to 2·5 times the weight of cellulose. The cellulose and nitric acid are heated together for an hour on the water-bath. The resulting oxycellulose is soluble in ammonia and is termed by the author β-oxycellulose If larger proportions of nitric acid are used lower yields are obtained, and corresponding quantities of oxalic acid are produced. By the action of bleaching powder on cellulose, Nastukoff obtained a different variety which he calls γ-oxycellulose.

β-oxycellulose combines with barium to form a salt containing about 5 per cent of the metal, while the corresponding salt of γ-oxycellulose contains only 1 per cent. The salts of β-oxycellulose and the substance itself are hard, whilst γ-oxycellulose and its compounds are brittle. A solution of the sodium salt of γ-oxycellulose gives a lustrous film on evaporation, whilst β-oxycellulose gives none Films may be obtained by evaporation in a desiccator, but of a totally different kind. The salts of β-oxycellulose have considerably less solubility after drying at 80° to 110° C, whereas the solubility of the salts of γ-oxycellulose is not altered by drying.

Knecht and Thompson (*J. Soc. Dyers and Col.*, 1920, p. 251) have described a method of preparation by means of which a yield of 94 to 95 per cent. of oxycellulose is obtained For this 30 grammes of filter-paper are pulped in 600 to 900 c c of 15° Tw. caustic soda. The pulp is thinned with water, mixed with a slight excess of dilute sulphuric acid, filtered and washed. The washed residue is suspended in from 600 to 900 c c of dilute sulphuric acid (10° Tw.) and mixed thoroughly A solution of 12 grammes of potassium permanganate in dilute sulphuric acid (10° Tw) is then added slowly by means of a tap funnel with constant stirring The addition of the permanganate should take from one to two hours, and the solution should be completely decolorised in four hours from the commencement of the experiment. The sulphuric acid has no action on the cellulose under these conditions The quantity of permanganate used gives one atom of oxygen for each $C_6H_{10}O_5$ molecule As the oxidation proceeds the pulp is gradually disintegrated, becoming finally a fine brown precipitate, the colour being due to oxide of manganese. The precipitate is filtered off, washed, and treated with hydrogen peroxide and dilute sulphuric to dissolve the oxide of manganese The colourless oxycellulose is then filtered off, washed, and dried at a low temperature.

Oxycellulose is also produced by alkaline oxidation of cotton Thus, if cotton be boiled with sodium hydroxide and a stream of air pressed through the boiling liquid, it is converted gradually into oxycellulose Peroxides in alkaline solution, or permanganates, produce the same result Even prolonged exposure to air is capable of bringing about the change, particularly in the presence of oxygen carriers such as traces of a copper salt. Lloyd (*J.S C I*, 1910, p 1450) found that salts of copper, cobalts, manganese, nickel, iron, and, to a small extent, chromium, all assist in the formation of oxycellulose, the action reaching a maximum, in the presence of moisture, at 50° C

The authors have examined cotton goods after exposure to a tropical sun which had become transformed almost completely into oxycellulose in patches In each of these oxidised portions distinct traces of copper were found

The constitution of oxycellulose is uncertain Cross and Bevan, owing to the fact that they could obtain only a yield of 30 per cent, suggested that a portion of the cellulose molecule is of a more resistant nature than the rest, but that it was always the same substance Faber and Tollens (*J S C.I*, 1899, p 1014) regard it as a mixture or a chemical compound of cellulose with a more highly oxygenated body which they term celloxin, $C_6H_{10}O_6$ or $C_6H_8O_6$, and which is the true oxycellulose not yet isolated They conclude that one such celloxin group is present with from one to four cellulose $C_6H_{10}O_5$ groups. Their oxycellulose yielded, on boiling with lime water, an insoluble residue of cellulose, and a dark solution from which saccharic and dihydroxybutyric acids were isolated

Nastukoff, as we have seen, regards oxycellulose as being of three different types according to the method of preparation differing in solubility, and which he designates γ-, β-, and α-oxycellulose respectively.

Other chemists are inclined to the view that oxycellulose is an adsorption product of cellulose with its products of hydrolysis or oxidation. Thus Harrison (*J. Soc Dyers and Col.*, 1912, p. 359) contends that this is so These adsorbed products are probably of an aldehydic nature in hydrocellulose and acidic in oxycellulose

Oertel (*J S C I.*, 1913, p 595) obtained a variety of oxycellulose by electrolysing a solution of potassium chloride containing cellulose in suspension The cellulose was attacked gradually and converted into soluble products When

about 60 or 70 per cent. had been dissolved, the residue, which consisted of oxycellulose, dissolved in a 10 per cent. solution of sodium hydroxide From a study of this compound, Oertel concluded that oxycellulose prepared by this method is an oxidised derivative of hydrolysed cellulose with a composition ranging from $(C_6H_{10}O_5)_6O$ to $(C_6H_{10}O_5)_{10}O$

Bancroft and Currie (*J.S C.I.*, 1915, p. 274) hold that oxycellulose is always the same product, in a qualitative sense, in whatever way it is prepared, and, having failed to convert the whole of the cellulose into oxycellulose in a single operation, they doubt whether pure oxycellulose has ever been prepared. According to their experience, oxycellulose is partly soluble in dilute alkali hydroxides, with a yellow colour, on heating. The residue is simply unoxidised cellulose The dissolved substance is precipitated by alcohol or acid and, after dialysis, it is readily soluble in water They regard this soluble substance as true oxycellulose, which may be a homogeneous substance. The distinctions made by Nastukoff between α-, β-, and γ oxycelluloses do not exist The so-called α-oxycellulose is simply unattacked cellulose more or less contaminated with its decomposition products, β- (alkali-soluble) and γ (water-soluble) oxycelluloses are the same substances in different states of aggregation. The copper-reducing power of oxycellulose is probably not characteristic and may be due to the presence of other decomposition products This property disappears on prolonged heating, without any change in the other essential characteristics of the oxycellulose.

Schwalbe and Becker (*J S C I*, 1920, 512A) are also of opinion that oxycellulose, however prepared, is simply a mixture of unchanged cellulose with its degradation products

Whatever the composition of oxycellulose may be, it is, however, generally agreed that it contains both ketone or aldehyde and carboxyl groups Further confirmation of this is found in a paper by Knecht and Thompson (*J Soc Dyers and Col*, 1922, p 132) They showed that in the initial stages of oxidation of cellulose the rise in the copper value is great For very small quantities of oxygen (as permanganate) it is almost proportional to the amount employed After about one-fourth of an atomic proportion of oxygen has been used, the rise in the copper value is less rapid, and after one half, very gradual The method employed was to treat cotton with cold sulphuric acid containing calculated amounts of permanganate

Atomic Portions of Oxygen used	Copper Number
1 atom	14 0
$\frac{3}{4}$,,	13 2
$\frac{1}{2}$,,	12 7
$\frac{1}{4}$,,	9 1
$\frac{1}{6}$,,	7 2
$\frac{1}{8}$,,	6 6
$\frac{1}{12}$,,	5 3
$\frac{1}{16}$,,	3 6
0 ,,	0 6

The authors conclude from these figures that in the early stages the oxygen is employed chiefly to produce or liberate aldehyde or ketone groups The fact that the formation of these groups, as measured by the copper number, does not increase proportionally as the oxidation proceeds, indicates that oxidising action is not simply conversion of hydroxyl into aldehyde groups. Probably carboxyl groups are also produced. This view is supported by the fact that the product of drastic oxidation of cellulose is largely soluble in sodium hydroxide. The ester reactions of oxidised cellulose prove that this acidic property is not due

to an increase in the number of reactive hydroxyl groups. It seems from these experiments that the composition of oxycellulose is variable, the proportion of aldehyde and carboxyl groups depending upon the extent of the oxidation

Schwalbe and Becker (*J.S.C.I.*, 1921, 807A) arrived also at a similar conclusion, namely, that oxycelluloses vary in character from those in which the aldehyde groups predominate to those where acid groups are in excess.

According to Birtwell, Clibbens, and Ridge (*J. Text Inst*, 1925, T. 13), the type of oxycellulose produced in bleaching depends chiefly upon the acidity or alkalinity of the hypochlorite solution used. On the alkaline side of the neutral point the acid groups predominate, and the product is characterised by solubility in sodium hydroxide, a high affinity for methylene blue, and comparatively low-reducing power indicated by the copper number When the reaction of the hypochlorite solution is on the acid side of neutrality, carbonyl or reducing groups predominate, and the product has a small affinity for methylene blue and is not so soluble in alkali, but has a greater reducing power indicated by the high copper number

Properties of Oxycellulose.—Oxycellulose is a white substance which gradually becomes yellow or brown when exposed to air. This change takes place rapidly under the influence of steam or dry heat. According to Muller (*J. Soc Dyers and Col*, 1922, p 209), hydrocellulose begins to turn yellow at 130° to 140° C. and scorches at about 150° C Oxycellulose does not become yellow till 150° C. are reached, whilst cotton requires a temperature of 180 C The presence of oxycellulose on cotton always causes considerable loss of strength or tenderness, and owing to the action of air gradual loss of colour

Owing to its acidic nature oxycellulose has a marked affinity for basic dyes, such as methylene blue and safranine, absorbing these rapidly from a cold solution. It has also a greater affinity for direct dyes than cotton It dissolves in alkalis, the solution becoming yellow on warming But the solubility varies with the method of preparation, depending upon the degree of hydrolysis and oxidation of the original cellulose Knecht's oxycellulose gives an intense yellow colour when boiled with N/100 sodium hydroxide, whilst with a 5N solution the colour is produced in the cold

Oxycellulose, compared with cotton, yields a relatively large amount of furfural when distilled with hydrochloric acid of 1·06 specific gravity This can be estimated in the distillate by treatment with phenyl-hydrazin, which converts it into an insoluble hydrazone Vignon obtained the following quantities of hydrazone per 100 grammes of material Bleached cotton, 1·8, oxycellulose, 2·1 to 3 5 The reaction is, however, not very distinctive, being shared to a considerable extent by other carbohydrates.

Oxycellulose is hydrolysed easily by acids. Vignon (*J S C I.*, 1900, p 1103) found that when oxycellulose was boiled for six hours with dilute sulphuric acid it gave more than four times as much sugar as the same weight of cotton The actual yield calculated as dextrose from the copper value was—

Purified cotton	3 29 per cent
Hydrocellulose	9·70 ,,
Mercerised cotton	3 51 ,,
Oxycellulose	14 70 ,,
Starch	98 60 ,,

The most interesting properties of oxycellulose are those associated with its aldehyde nature It acquires a deep yellow colour when soaked in a solution of phenyl-hydrazin in acetic acid Knecht's oxycellulose assumes at once a magenta colour when placed in Schiff's decolorised magenta solution. When heated with

a solution of potassium ferricyanide oxycellulose reduces some of the ferric to ferrous iron, and a precipitate of Prussian blue is produced. The reaction will take place also in the cold

When methylene blue is heated with oxycellulose, in the presence of sodium hydroxide, the dye is reduced to the colourless leuco-compound. According to Knecht, an ordinary vat of soluble reduced indigo may be prepared in the same way Owing to this property of reducing dyestuffs to their leuco-compounds, oxycellulose may exercise an important effect in dying Knecht (*J Soc. Dyers and Col*, 1921, p 76) records the following experiments· A known weight of oxycellulose powder was heated with a solution containing excess of dyestuff for one hour under a reflux condenser, in the presence of sodium hydroxide The solution was then filtered and the dye remaining in the filtrate determined by titration In some cases the dyestuff destroyed by the oxycellulose was more than that necessary to produce a full shade in dyeing, but the oxycellulose remained undyed although its copper value was reduced from 11 to 0·9 Direct cotton colours, like primuline, which are not affected by reducing agents, dye the oxidised cellulose immediately

But the most important of the properties of oxycellulose is its reducing action on Fehling solution This, of course, is owing to the presence of CO groups If over-bleached cotton, containing oxycellulose, be boiled with Fehling solution for about ten minutes it becomes red, owing to the deposition of cuprous oxide, while more of the precipitated oxide will be found suspended in the liquid. If the experiment be carried out quantitatively under standardised conditions, a measure of the degree to which the cotton has been oxidised can be obtained. This is perhaps the most important determination in the analysis of cotton or cellulose It is known as the determination of the " copper number "

The Copper Number. -This is defined as the weight of copper reduced from the cupric to the cuprous state by 100 grammes of the material, under standard conditions Pure cellulose has an insignificant copper number, never exceeding 0 5 For Knecht's oxycellulose the number is 14·2 Oxidised cotton may give, therefore, any value between 0·5 and 14·2 according to the degree of oxidation According to Clibbens and Geake (*J Text Inst*, 1924, T 27), 0·2 may be regarded as the maximum value for well-bleached goods

The method was suggested, first, by Schwalbe His method (*J S C I*, 1907, p 548) is as follows Two portions of about 3 grammes each of the material are weighed One portion serves for the determination of the dry substance. The other is cut into small pieces, without drying by heat, and is placed in a flask, together with 100 c c of Fehling solution and 200 c c of water. The contents of the flask are boiled under a reflux condenser for fifteen minutes, with frequent agitation The time of boiling is measured from the commencement of ebullition The hot liquid is then filtered by the aid of a pump and the residue containing the cuprous oxide is washed with boiling water The cuprous oxide is then dissolved in nitric acid and the copper determined by a suitable method, preferably electrolytic From the weight of copper obtained the " copper value," *i e* the percentage of metallic copper on the dry material, is calculated. Schwalbe gives the following copper values for various normal and altered celluloses –

Surgical cotton-wool	1 6
Mercerised bleached cotton	1 9
Artificial silk (*glanzstoff*)	1 1
Hydrocellulose	5 2
Parchment paper	4 2
Oxycellulose .	7 9
Over-bleached wood pulp .	19 3

Schwalbe's method has one disadvantage Cellulose adsorbs copper from Fehling solution, which is difficult to remove by washing with hot water. The adsorbed and unreduced copper must be determined and deducted from the copper value given by Schwalbe's method. This may be done by treating a similar piece of cotton with cold Fehling solution. The sample is then washed with boiling water and the residual copper estimated It is assumed that the amounts of copper adsorbed from cold and boiling Fehling solution are identical, though the assumption cannot be proved.

Knecht and Thompson's method (*J. Soc Dyers and Col*, 1920, p. 255) avoids these difficulties completely The cuprous oxide is dissolved in an acidified solution of a ferric salt, *e g.* iron alum, when it reduces its equivalent of iron. The ferrous salt thus produced is then titrated with standard permanganate solution. The following procedure is recommended. The boiling with Fehling solution is carried out as in Schwalbe's method The liquid is then decanted through a Gooch filter and the residue washed with hot water The filter and its contents are then transferred to a vessel containing from 1 to 2 grammes of iron alum dissolved in dilute sulphuric acid and stirred till the cuprous oxide is dissolved. The solution is then filtered and the residue washed The ferrous sulphate in the filtrate is now titrated with decinormal permanganate solution Dry oxycellulose, treated in this manner, gives a copper value of 14·2

When oxycellulose is boiled with sodium hydroxide it is decomposed with the formation of bodies having no reducing action on Fehling solution. It is possible that this occurs to a certain extent when it is boiled with Fehling solution. The same authors have suggested an alternative method of estimation in which the oxycellulose does not come into contact with boiling sodium hydroxide solution It depends upon the precipitation of cuprous thiocyanate The copper solution used is made by dissolving 100 grammes of anhydrous sodium carbonate and 125 grammes of potassium thiocyanate in about 800 c c of water. A solution of 18 grammes of crystalline copper sulphate is then added and the solution made up to 1 litre The cotton is boiled with this reagent with the addition of some sodium carbonate The mixture is filtered and the precipitate and residual cotton washed The washed residue is warmed with semi-normal sodium-hydroxide solution, and the cuprous hydrate formed is filtered and washed till free from thiocyanate The filter and its contents are then treated with iron-alum solution and titrated as in the previous process

A rather similar method, due to Braidy, is also described by Koehler and Marqueyrol (*J S C I*, 1922, 323A) In this the cotton is simply heated with a mixture of copper sulphate and sodium bicarbonate, the precipitated cuprous oxide being dissolved with ferric sulphate and titrated with permanganate

This method has been investigated very carefully, in comparison with those in which Fehling solution is used, by Clibbens and Geake (*J. Text Inst*, 1924, T 27), and is recommended as avoiding—

1 The error due to adsorbed copper.
2 That due to anti-reduction of Fehling solution when boiled.

The following details of Braidy's method are taken from the paper of Clibbens and Geake —

The following solutions are required.—

(*a*) A hundred grammes of pure crystalline copper sulphate dissolved in 1 litre of water
(*b*) Fifty grammes of sodium bicarbonate and 350 grammes of crystallised sodium carbonate dissolved in 1 litre of water.

(*c*) A solution containing 100 grammes of iron alum and 140 c c. of concentrated sulphuric acid per litre.
(*d*) Standard N/25 potassium-permanganate solution.

Immediately before use, 5 c.c. of solution (*a*) are run from a burette into 95 c c. of solution (*b*), the mixture is raised to the boiling point and poured over 2·5 grammes of the material to be tested contained in a conical flask of a capacity only slightly more than 100 c c The cotton is distributed through the liquid by means of a glass rod and any air-bubbles present allowed to escape. The flask is then immersed in a constant level water bath which is kept boiling rapidly The flask should be immersed deeply in the water and care taken to cover the top of the bath sufficiently to prevent cooling of the reaction mixture by currents of cold air The flask is allowed to remain in the boiling water for exactly three hours, the contents then filtered with suction, and the cotton, impregnated with the cuprous oxide, is washed, first with dilute sodium-carbonate solution and then with hot water

The cuprous oxide is then dissolved, by treating the cotton on the filter with 15 c c of solution (*c*), and then by another 10 c c , and a third 10 c c if necessary The cotton is then washed with 2N sulphuric acid, and the combined filtrates and washings are titrated with standard potassium permanganate solution, approximately N/25, corresponding to about 2·5 mgm of reduced copper per cubic centimetre The end-point is sharp and stable

For accurate results the details must be followed carefully, and neither more nor less than 2 5 grammes of cotton should be used

Kauffmann (*J Soc Dyers and Col.*, 1924, p 128), in an attempt to find a quicker and more reliable method of determining the degree of oxidation of cellulose, tried to modify the qualitative reactions of this substance in such a way as to permit of their quantitative application. With the majority of these reactions, such as the varying intensity of colour obtained on dyeing with methylene blue, of the yellow colour obtained with phenyl-hydrazin, and of the blue coloration produced by the reduction of indanthrene yellow to dihydroflavanthrene hydrate. the effect of the different mechanical conditions of the materials prohibited their application Although the use of an ammoniacal caustic alkaline silver solution appeared to be capable of quantitative application, the results obtained by another method were so favourable that the modification of this reaction was not continued

The new method consists in boiling the cellulose with aqueous caustic soda, and subsequently determining the quantity of permanganate required to oxidise the organic matter present in the solution so obtained The process finally adopted was as follows The sample (1·0 gramme of fabric) was boiled for thirty minutes with 150 c c of caustic soda of 7 4° Tw with frequent addition of distilled water to conserve the volume. This liquor, and the water in which the sample was well washed, were transferred to a 500-c.c measuring flask and diluted to the mark , 100 c c of this solution (50 c c when using highly oxidised celluloses) were acidified with 25 c c 10 per cent sulphuric acid mixed with 10 c c N/10 permanganate and boiled for ten minutes On cooling to 70° C excess of oxalic acid was introduced, and finally permanganate was added until a faint pink colour was obtained The total volume of permanganate, less the equivalent of the oxalic acid, gave the quantity of permanganate used

This treatment did not account for all the oxidisable matter in the cotton, and it was necessary to repeat the process until the quantity of permanganate required was constant This amount of permanganate was found to be required

by the oxidisable matter extracted by the alkali from the cellulose itself, and was termed the base value This must be subtracted from all results. For example, in one series, the following results were obtained —

Boiling	Permanganate used c c	
	Total	By Oxidised Cellulose
1	18 0	11 5
2	13 3	6 8
3	11 0	4 5
4	8 0	1 5
5	7 5	1 0
6, 7	6 5 (base value)	0 0
		Total 25 3 c c

This volume of 25 3 c c was termed the permanganate number When a constant volume of permanganate is required it is a certain indication of a pure cellulose, and even with samples which failed to show any of the usual qualitative tests for oxidised cellulose, results were obtained by the permanganate method which indicated a slight degree of oxidation

Sizing must be removed from fabrics before subjecting them to this method of estimating the degree of oxidation, and for this purpose fats and waxes were removed by extraction with ether in the usual way, and starches by steeping for two hours in a 1 per cent aqueous diastafor solution at 65° C , followed by thorough washing in cold water, and subsequent boiling with distilled water This brings about the complete removal of starch and diastafor, whilst neither this treatment nor the ether extraction affects the oxidised cellulose

Ristenpart (*J S.C I* , 1924, 291B) describes the following method of using methylene blue as an indicator for the quantitative determination of oxy cellulose

According to Ostwald's notation, a *matt surface of barium sulphate* is used as a standard for " normal white," and 100 stages of grey are distinguished between this and black On this scale a commercial bleached cotton has a value of 70 to 80 degrees of white Damage during bleaching is indicated by increased affinity for methylene blue, and a comparison may be obtained in the form of a ratio, Q, between the degree of " white " of the original sample and the degree of " white " in the sample dyed with methylene blue If this ratio be Q in the bleached goods and Qu in the unbleached, then the methylene blue value is expressed as the difference produced by bleaching $M=(Q-Qu)/Qu$ The dyeing is performed by treating 5 sq cm. of the fabric with 500 c c of a cold 0·001 per cent solution of methylene blue for ten minutes, rinsing, and drying in contact with a smooth surface, then determining the degree of " white " Practical trials with hypochlorite bleach showed that the methylene blue value increases with the concentration of chlorine, also with rise in the temperature of bleaching It is not increased by alkalinity of the bleach liquor and only slightly by acidity Cotton may be regarded as free from oxycellulose if its methylene blue value is less than 20.

Further details about this test are given in Chapter XXIV.

The Identification of Hydrocellulose and Oxycellulose.—The identification of these compounds is often of importance Unfortunately, the distinction between the two is a matter of considerable difficulty This is particularly marked in the case of the products of the hydrolysis caused by drying mineral acids into cotton Before tabulating the various quantitative tests an important paper by Knecht and Thompson (*J Soc Dyers and Col*, 1921, p 270) must be referred to They found that a twofold action takes place when dilute sulphuric acid is dried into cotton The cellulose is partly hydrolysed. This results in reduction of tensile strength, and there is a fixation of some of the acid in the fibre which acts as a mordant for basic dyestuffs When 1 per cent sulphuric acid is dried into cotton both of these actions take place The cotton becomes tendered and acquires a great affinity for methylene blue, rhodamine B, crystal violet, etc even after prolonged washing with water or alkali But it has a decreased affinity for direct dyestuffs, particularly diamine sky-blue The increased affinity for methylene blue does not depend upon the degree of tendering Cotton boiled for an hour with 0 5 per cent sulphuric acid has a diminished tensile strength, but its affinity for methylene blue is not increased but is slightly less than that of the unboiled cotton No sulphuric acid is fixed When cotton is tendered by the prolonged action of dilute acids without allowing the acid to concentrate, there is no increased affinity for basic dyestuffs But when the acid is allowed to dry into the cotton (*i e* to concentrate) in the presence of air oxidation takes place, and this is accompanied by an increased affinity for methylene blue Further, the treated cotton has a marked affinity for the leuco-compounds of such colours as methylene blue, but the affinity of oxycellulose is only slight The products of the action of sulphuric acid on cotton differ, therefore according to whether drying in and oxidation occur or not

These products may be distinguished by means of diamine sky blue after treatment of the cotton with sodium hydroxide solution Both sulphuric acid treated and oxidised cotton resist dyeing with diamine sky-blue But, after boiling with a 5 per cent solution of sodium hydroxide, the oxidised cotton (*i e* oxycellulose) takes up the dyestuff, while the cotton treated with acid without drying does not That is, cotton which has acquired an increased affinity for methylene blue and has a decreased affinity for diamine sky blue, after treatment with sulphuric acid, does not contain oxidised cellulose but sulphur which is not removed by washing with boiling water or alkali Tendering which is unaccompanied by an increased affinity for basic dyestuffs may be caused by (1) hydrochloric acid, or (2) the prolonged exposure to hot dilute sulphuric acid without drying

Qualitative Tests for Hydrocellulose and Oxycellulose.

1 *Action of Heat*.—Cotton which is free from hydro or oxy cellulose may be heated to a temperature of from 130° to 150° C without undergoing any alteration in colour But according to Justin Mueller (*J S C I*, 1922, 9A), hydrocellulose becomes brown and oxycellulose pale yellow at those temperatures

2 *Freiberger's Test*.—The material is treated with a solution of sodium ricinoleate and steamed In the presence of oxycellulose a yellow colour is produced, the depth of which is directly proportional to the amount of oxycellulose present

3 *Methylene Blue Test*.—Both hydrocellulose and oxycellulose are characterised by the power of absorbing basic dyes from a cold aqueous solution Cotton, on the contrary, has no affinity for these colours. If the cotton is soaked in a

cold aqueous solution of methylene blue or safranine and then washed it will remain coloured if oxycellulose is present, and the depth of the colour gives some indication of the amount of oxycellulose The colour is removed by boiling with water The test requires some experience, since all the bleached cotton has an increased affinity for dyes

4. *Knapp's test* depends upon the increased affinity which cotton containing oxycellulose has for the direct or substantive dyes The material is dyed by boiling with a solution of benzo-purpurin This dye is very sensitive to acids The dyed sample is placed in a beaker with some distilled water and treated with dilute hydrochloric acid till the shade becomes blue It is next rinsed with hard water to neutralise the acid, when the red colour reappears on the cotton Oxycellulose, however, remains blue-black in colour

5 *Knecht's test*, which is somewhat similar in principle, has also the advantage of distinguishing between hydro- and oxy-cellulose Both of these compounds have a decreased affinity for direct dyes such as diamine sky-blue If a sample of the cotton when dyed with a solution of this dye shows patches which resist the dye, then it may be concluded that either hydrocellulose or oxycellulose is present, or that both are A fresh sample of the cotton is now boiled in a 5 per cent solution of sodium hydrate, washed, and dyed as before with diamine sky blue Oxycellulose now absorbs the dye, but hydrocellulose either does not or has a decreased affinity That is, cotton which has an increased affinity for methylene blue, and, after boiling with sodium hydrate, a decreased affinity for diamine sky-blue, cannot contain oxycellulose

6 *Ermen's Test* —A suspension of indanthrene yellow is prepared by dissolving the paste in strong sulphuric acid, pouring the solution into cold water, and neutralising A few drops of this suspension are added to some 10 per cent solution of sodium hydrate The material to be tested is saturated with the mixture and lightly squeezed It is then held over a beaker of briskly boiling water If either hydrocellulose or oxycellulose is present a deep blue stain appears within one minute The remainder of the sample will, if well bleached, show no blue colour for at least five minutes If, after steaming, the sample is washed, scoured, again washed, and then rubbed with soap, the unaffected dyestuff is readily removed, but where reduction has taken place, the colour is fixed firmly

7 *Schiff's test* depends upon the presence of an aldehyde group in oxycellulose A solution of magenta is treated with sulphurous acid or a solution of sodium bisulphite till it is just decolorised If cotton containing oxycellulose is immersed in this solution it acquires a magenta colour

8 *Phenyl-hydrazin Test* —Oxycellulose acquires a yellow colour when treated with a solution of phenyl-hydrazin or para-nitro phenyl-hydrazin in acetic acid.

9 *Dutz's Test* - Both hydro- and oxy-cellulose reduce Nessler solution at ordinary temperatures If cotton containing either of these is immersed in the cold solution it, at first, becomes brown, but rapidly changes to pale or dark grey owing to the reduction of the mercuric salt

10 *Action of Alkalis* - - Oxycellulose becomes yellow when boiled with N/100 sodium-hydroxide solution The same result is obtained by soaking in a cold, stronger solution of the reagent Some oxycelluloses are soluble in caustic alkalis In this case yellow solutions are produced

11. *Schwalbe's Test.*—Both hydrocellulose and oxycellulose reduce Fehling solution The sample is first boiled with water to remove soluble reducing bodies. It is then placed in a mixture of equal volumes of Fehling solution and distilled water and boiled gently for about fifteen minutes. If hydrocellulose or oxy-

cellulose is present the cotton becomes red owing to the deposition of cuprous oxide.

12. *Schwalbe and Becker* recommend the following test as being capable of distinguishing between hydro- and oxy-cellulose. Some of the sample is made into a paste with distilled water and a drop of methyl-orange solution is added. In almost all cases the liquid remains yellow, but with strongly acid oxycelluloses it becomes reddish orange. A few cubic centimetres of brine are added. In the case of ordinary cellulose or hydrocellulose the colour is almost unchanged, while if oxycellulose is present it is a deep wine-red. The method may be used quantitatively by titrating with N/100 sodium hydroxide, but in this case methyl red should be used as the indicator, as the end-point with methyl orange is not sharp.

Harrison's Test — Silver nitrate is added to a solution of sodium thiosulphate, with vigorous stirring, and then sodium hydroxide solution, so as to obtain a liquid containing 1 per cent of silver nitrate, 4 per cent. of sodium thiosulphate, and 4 per cent of sodium hydroxide The suspected material is boiled or padded with this solution and then steamed The parts containing hydrocellulose or oxycellulose become stained This effect is increased if the material is first heated with a 1 per cent solution of phenyl-hydrazin in glacial acetic acid and washed thoroughly with dilute acetic acid

Cellulose Peroxide. Oxycellulose must be regarded, as has been shown above, as an oxidation product containing both ketone and carboxyl groups But under certain conditions it appears, also, to form an oxide which has the properties of a peroxide, *i.e.* contains loosely combined oxygen This body is termed "cellulose peroxide" It appears to have been studied first by Cross and Bevan (*J S C I*, 1907, p 44) They found that cellulose fabrics, after bleaching with bleaching powder without the subsequent use of an antichlor, retained the property of liberating iodine from potassium iodide for a much longer time than was consistent with the survival of traces of hypochlorites Such fabrics retained an acid reaction and oxidising properties (towards potassium iodide) even after exhaustive washing with distilled water After removing the acidity, by washing with hard water, the reaction with potassium iodide remained But boiling with water or treatment with an antichlor destroyed the oxidising property, as did also dry heating at 100° C This drying was accompanied by tendering Cross and Bevan concluded that a "peroxidised" derivative of cellulose was formed But these effects could have been produced also by chloramines formed by the action of chlorine on unremoved proteins Ditz (*J S C I*, 1907, p 988) observed that the same phenomenon can be produced by heating cellulose with an acid solution of a persulphate slowly up to a temperature of 80° C and then cooling gradually. When heated at 100° C with the persulphate solution the cellulose exerts a powerful "activifying" action on the decomposition of the persulphate Oxygen and carbon dioxide are evolved together with an irritating gas This "activification" was attributed by Ditz to the momentary production of cellulose peroxide, but in this case, owing to the high temperature of the reaction, the cellulose itself did not retain the properties of a peroxide. When the action was carried out in the absence of acid the peroxide properties of the product were feeble. Using a 10 per cent. solution of persulphate and dilute sulphuric acid (1 '4), 0·015 per cent of oxygen was found to be fixed in one case. The products obtained with potassium persulphate were less active than those given by the ammonium salt. The cellulose peroxide (*J.S.C.I.*, 1907, p. 1026) has the properties of an insoluble acid as recorded by Cross and Bevan. It liberates iodine from a mixture of potassium iodide and iodate quite apart from its active oxygen property When suspended

in water, the peroxide shows the ordinary yellow colour on the addition of methyl orange, but if a solution of a neutral salt, *e.g* a chloride, be added the solution turns red. The acidity of the peroxide is not destroyed, like the active oxygen, by boiling with water for two minutes. In fact, the two properties appear to be independent of each other When the peroxidised cellulose was heated with a 10 per cent solution of sodium hydroxide partial solution occurred, accompanied by the production of a golden-yellow colour The peroxidised cellulose also reduced Fehling solution. These facts indicate the presence of oxycellulose Hence Ditz concluded that the products of the action of ammonium persulphate on cellulose in presence of sulphuric acid are—

1. A peroxide
2. A free acid, possibly acid cellulose.
3. A reducing substance, probably oxycellulose
4 Unaltered cellulose

The cellulose peroxide in the products of the reaction was only stable for a short time in the moist condition, but when dried over sulphuric acid after treatment with alcohol and ether it became relatively stable Hydrogen peroxide does not yield a peroxide under similar conditions In further investigations, *Ditz (J S C I, 1908, p 1129) found that when cellulose is heated with acidified* ammonium persulphate an irritating odour of "active oxygen" is observed, and the gases obtained liberate iodine from potassium iodide Acidified persulphate alone yields a little of the same product, but much less than when cellulose is present It would appear that cellulose peroxide is an unstable intermediate product, breaking down at the moment of formation with liberation of active oxygen. It is possibly an intermediate product between cellulose (alcohol) and oxycellulose (aldehyde) Dorée (*J Soc Dyers and Col*, 1913, **29**, 205) investigated the action of ozone on cotton-wool When this was exposed in the dry state to a current of ozonised oxygen containing 1·5 per cent by weight of ozone, it acquired a faint odour, became acid to moist litmus paper, and liberated iodine from potassium iodide The last property disappeared when the product was heated to 80° C or kept for fourteen days, but the acidity was permanent. These properties indicated the formation of a peroxide similar to that described by Ditz The following properties of cellulose peroxide were given It is decomposed when treated with water, hydrogen peroxide being slowly produced Exposure to air for two hours at a temperature of 37° C reduces the activity, while an exposure for two hours at 95° C practically destroys it If the material is kept in a vacuum, the activity persists for several weeks The peroxide acts strongly on a photographic plate in the dark The active substance is volatile, the plates showing a band of reduced silver when fixed 5 mm above the cellulose threads This photographic activity is probably due to nascent hydrogen peroxide, formed by the action of water on the cellulose peroxide Dorée considers that the peroxide oxygen attaches itself possibly at a tertiary hydroxyl, or more probably at a carbonyl group The cellulose peroxide decomposes in the presence of water, forming an aldehyde (oxycellulose), or it may act as a catalytic agent, causing further oxidation From the commencement of the ozone action carbon dioxide is produced and acid developed in the cotton The acidity can be removed either by boiling with water or by neutralisation After removal of the acid the residue (80 to 90 per cent) has the properties of oxycellulose It reduces Fehling solution, has an increased affinity for methylene blue, an increased copper number, and an increased solubility in alkali Mercerised cotton is attacked much more readily than

ordinary cotton, and viscose silk is intermediate between the two These results are illustrated in the following table :—

	Cotton-wool		Mercerised Cotton-wool		Mercerised Yarn, 2/60, Grey (Tension)		Viscose Silk, 120 Deniers	
	Normal	After 24 Hrs Ozone	Normal	After 24 Hrs Ozone	Normal	After 24 Hrs Ozone	Normal	After 24 Hrs Ozone
Loss in weight per cent		12 0		7 0		.		4 5
C per cent .	44 4	43 5	43 2	43 5			44 6	44 4
Methylene blue absorption	0 3	2 1	0 4	3 1		2 3	1 6	1 8
Copper number	1 2	16 9	1 7	24 0		9 6	3 0	15 5
Loss in 10 per cent KOH		64 0		57 0				50 0

In all cases there was a rapid decrease in tensile strength, indicating tendering.

CHAPTER IX.

SPECIAL PROPERTIES OF COTTON.

Action of Heat.—Cotton may be heated, in the dry state, for a short time to a temperature of 150° C without undergoing decomposition, but, if the heating be prolonged, it becomes yellow or brown At the same time, oxygen is absorbed, oxycellulose is formed and the tensile strength becomes less When heated at temperatures much above 150° C, cotton is decomposed with the production of various bodies, including acetic acid If either hydrocellulose or oxycellulose be present, cotton becomes much more sensitive to the action of dry heat Hydrocellulose begins to turn brown at 130° C, while at the same temperature oxycellulose becomes yellow Moist heat is not so destructive in its action, but when cotton is heated for a long time with steam, in the absence of air, it is changed gradually into hydrocellulose, the velocity of the reaction depending upon the temperature

Knecht (*J Soc Dyers and Col*, 1920, p 195) found that prolonged heating, at comparatively low temperatures (80° C), produced the same effects as heating for a shorter time at a higher temperature Knecht and Muller (*J Soc Dyers and Col* 1925, p 45) arrived at the following conclusions

1 Prolonged heating of cotton yarn at 90° C reduces its tensile strength and increases its copper number

2 Heating in a vacuum causes less deterioration than heating in the presence of air

3 The copper number does not increase in proportion to the loss of tensile strength, except in the case of mercerised cotton

4 The discoloration produced is not commensurate with the deterioration

5 Mercerised cotton is more sensitive to the action of heat than ordinary cotton

6 Traces of volatile acid are formed when cotton is heated in a sealed tube at 90° C and, even when heated in evacuated tubes, the copper number increases and the yarn becomes tender, the aqueous extract of the heated cotton indicating the presence of a soluble carbohydrate

The Action of Air.—The action of air on cotton is associated very closely with the phenomenon known as ' weathering " A perfect textile fibre should be permanently unaltered however long it is exposed to atmospheric influences In practice no fibre reaches this ideal although some, like cellulose acetate, are more durable than others For want of a better term this gradual disintegration of textile fibres which takes place when they are kept for prolonged periods is known as " weathering " In the case of cotton, it is a distinctly marked process which occurs when the material is exposed to air, both in the presence and absence of light Weathering is accelerated, greatly, by faulty processes used in the preparation of the goods Thus, if traces of a metallic oxide, such as copper

oxide, are present, which can act as oxygen carriers, the production of oxycellulose becomes quite rapid This is, of course, accompanied by the production of tenderness and also of yellowing In investigating the action of air the following factors must be considered, viz —

1 The action of light
2 The action of oxygen
3 The action of traces of ozone and hydrogen peroxide
4 The effect of moisture
5 The effects of temperature and pressure.
6 The action of aerial micro-organisms

The action of light on cotton was studied by Dorée and Dyer (*J S C I*, 1917, p. 211) by exposing cotton fabrics to the action of light from a Cooper-Hewitt mercury vapour lamp at a temperature of from 30° to 35° C This lamp produces a large concentration of ultra-violet rays It was observed previously, by Witz, that while blue rays of light cause the production of oxycellulose, neither yellow nor red rays have any action Dorée and Dyer used a single-ply cotton fabric such as is employed for the envelope of an airship. They found that, after exposure for a week to the rays of the mercury vapour lamp, it acquired a biscuit-yellow colour and showed a greatly decreased tensile strength Not only did sodium hydroxide produce a yellow colour, but dissolved much of the exposed portions of the fabric Comparisons of the exposed portions of the fabric with hydrocellulose, prepared by the action of sulphuric acid on cotton, showed considerable differences, whereas the properties of the exposed material resembled closely those of oxycellulose Thus, when treated with a cold 1 per cent solution of sodium hydroxide, much was dissolved and the characteristic yellow colour given by oxycellulose was produced It reduced Fehling solution, gave furfural when distilled with hydrochloric acid, and had an increased affinity for methylene blue These results are summarised in the following table —

	Unexposed Fabric	Exposed Fabric
Loss of weight when boiled in sodium hydroxide—		
For 5 minutes	Per cent 0 00	Per cent 9 50
For 60 minutes	1 00	13 60
Copper number	0 62	4 00
Furfuraldehyde	0 20	1 34
Methylene blue absorption	0 70	1 50

The tensile strength of the exposed portions of the fabric had entirely gone, and transverse cracks with the occasional swollen places, similar to the effects produced by excessive action of alkali, were noted. The affected part was much more absorbent, and wetted out more readily than the unaffected part of the fabric Dorée and Dyer concluded that ultra-violet light, in the presence of moisture and air, acts in two ways

1 By some specific physical action, causing disintegration of the cellulose
2 By the development of ozone at the surface of the fabric, which is known to convert cellulose into alkali-soluble products having the properties of oxycellulose.

The action of ozonised air upon cotton and the production of cellulose peroxide

has been described already (p 119) The tendering action of ozonised air on cotton yarn is shown in the following table given by Doree and Dyer It refers to an Egyptian 1/40 cotton, the original tensile strength being taken as 100

Time of Exposure to Air containing 1 to 2 per cent of Ozone	Breaking Strength
0 5 hours	100
1 0 „	99
3 0 „	91
6 0 „	88
12 0 „	53

Turner (*J Soc Dyers and Col*, 1920, p 165) also investigated the influence of atmospheric exposure on the properties of cotton fabrics, using a Westinghouse Cooper-Hewitt quartz mercury arc lamp Special precautions were taken to determine (1) whether or not the loss of tensile strength was more marked at the point where the thread used had been exposed to the action of light, (2) to use light of a particular wave length

Turner s experiments pointed to the following conclusions

1 For wave lengths greater than 3660 A U there is no destructive effect That is, it is probably safe to conclude that visible light has little, if any, tendering action

2 There is apparently no limit to the action of light with shorter wavelengths

3 The effect of a sheet of glass which cuts off the spectrum below 3990 A U is much greater for the mercury arc than for sunlight

The removal of oxygen from the atmosphere surrounding the fibres reduced greatly, but did not entirely inhibit, the destructive action of the light The presence or absence of moisture made no difference It should be noted that if in the complete absence of oxygen disintegration still takes place, the conclusions of Doree and Dyer, with regard to the intensified action in the presence of air and the possibility of the formation of ozone, receive important confirmation The following notes are taken from *Researches on Cellulose*, by Cross and Doree, vol iv p 123 Lynam has shown that the light causing direct formation of ozone must have a wave length of less than 1850 A U , and that it is absorbed completely by 1 mm of air at ordinary pressure No appreciable quantity of ozone can be formed at the earth's surface It is therefore difficult to account for its formation in the linen threads But Lindemann, taking into account the refractive index of linen (1 53) and the dielectric constant of the medium, has worked out that the most destructive portion of the spectrum should be that with a wave length of 3230, which is in fair agreement with the observed results

The influence of the combined action of bacteria, moisture, and light on cotton and linen was investigated also by Turner (*J Soc Dyers and Col*, 1920, p 165) He found that the rate of deterioration was the same, both at Berbera, which has a very dry climate, and at Malacca, where the climate is humid and there is much rain But at both places the rate of deterioration was greater than at Farnborough

At Malacca there was much growth of mould, which accounted for part of the deterioration, and it was found that cotton is less sensitive to light than flax but more sensitive to moulds

Aston (*Reports and Memoranda*, No 396, 1917) states that there is evidence that ozone, or active oxygen, is the most important factor in the destruction of linen fabrics by light, but it is impossible for sunlight to produce much ozone from atmospheric oxygen at a point near the earth's surface He accepts, therefore, a possible explanation suggested by Lindemann The most effective frequency for ionising oxygen, as found from a quantum relation, corresponds to a wave length λ 1380A From an approximate deduction of the dielectric constant of linen, it is calculated that this frequency for molecules of oxygen in intimate contact with, or adsorbed by the linen is λ=3230A, a result which Aston considers to be in good agreement with his own observations, though the latter can only be regarded as indicating that tendering is produced by light of wave lengths less than λ=3230A The theory, moreover, appears to rest on the assumption that ionised oxygen is responsible for the production of ozone, or, alternatively, that ionised oxygen is the cause of tendering

The action of bacteria and moulds on cotton will be dealt with in Chapter X

The Action of Mechanical Forces on Cellulose.- This is a property difficult to classify, but which has some importance in the mechanical operations of finishing Fort (*J S C I*, 1918, 121A) observed that if, owing to the breaking of a traverse during beetling (*q v*), the hammers fall continuously on the same sector of the cloth, the temperature rises and conditioning moisture is lost In the case observed, that portion of the cloth subjected to this abnormal mechanical treatment was completely ruined, and a deposit, resembling lumps of starch, was obtained, which could be crushed easily to a fine, smooth powder with a slight tendency to break in layers The product contained no undestroyed fibres, but occasional small shreds of cuticle were found The powder had the chemical properties of cellulose and gave negative results for hydrocellulose and oxycellulose When treated with sodium hydroxide solution of 52 Tw the particles swelled but did not dissolve The powder gave no reaction with iodine, but, after treatment with hydrochloric acid, the yellowish brown colour due to dextrin was obtained It was evident, from the appearance of the cloth, that heat played a large part in the reaction, and it was found that a temperature of 200° C was reached in the hottest part The examination of the powder by Cross (*J Soc Dyers and Col*, 1919, p 27) showed that a large amount of alkali-soluble β cellulose had been formed and the microscopic structure of the powder was quite different from that of ordinary shredded cellulose Another case of mechanical breakdown of a cotton rope used for power transmission is recorded also by Cross, in which the yarn was converted at the core into rounded hyaline masses of small dimensions It was concluded that the fibrous colloids had been transformed through a phase of hydrate "fusion" into the structureless form in question, the only possible causes being of the mechanic l physical order When cellulose is treated in a papermaker's beater it swells and becomes more hydrated These swollen masses or gels dry to hard, horny products which swell again in a damp atmosphere

The Action of Water.—Cold water has no chemical action on cotton, but prolonged soaking causes the hairs to swell up and temporarily lose the natural twist When the cotton is redried, the twist reappears Harrison (*Second Report on Colloidal Chemistry*, p 54) states that cotton, when subjected to stress in the dry condition, acquires an increased power of double refraction, which persists after the stress is removed This increased double refraction shows the presence of extra internal stresses resulting from the deformation. When such cotton is soaked in cold water, these internal stresses disappear and the fibres regain their original shape. When compressed in boiling water, the fibres

become permanently deformed and no internal stresses are produced Soaking in cold water dissolves some of the impurities present, both organic and inorganic Boiling water has a greater solvent action Lester (*J S C I*, 1902 p 388) gives the amount as 2 per cent, and concluded that these bodies extracted by boiling water were largely responsible for the hygroscopic nature of cotton Knecht (*J S C I*, 1911, p 1007) found that Egyptian cotton, after removal of fatty matters and wax by means of petroleum ether and alcohol, gave from 1 48 to 1 61 per cent of extract when treated with water In a later paper (*J S C I*, 1919, 7A) it was found that the aqueous extract was rich in mineral matter, a considerable portion of which consisted of potassium salts Upon dialysis the aqueous extract was separated into two portions The diffusible constituents were very hygroscopic, and rich in potassium salts The undiffusible residue yielded, on evaporation, a non hygroscopic brittle resinous substance Aqueous extraction removed from 14 to 16 per cent of the total nitrogen Grace Calvert (*J Chem Soc*, 1866, **20**, 303) showed that practically the whole of the phosphorus was removed from cotton by extraction with water Herzfeld and Klinger (*J Text Inst*, 1923 T 79) proved that a 2 per cent suspension of cellulose in water is partially decomposed by heating for four hours at 138° C The portion dissolved by water gave an osazone resembling that obtained from maltose Schwalbe (*J S C I*, 1910, p 750) showed that only cellulose which has already been affected by excessive bleaching, etc undergoes hydrolysis when heated with water under pressure, and Schwalbe and Robinoff (*J S C I*, 1911, p 277) found that up to a temperature of 150° C pure cellulose was affected very little, and that this appears to be a "critical" temperature Tauss (*J Text Inst*, 1923, T 78) had previously determined the amount dissolved from Swedish filter paper when heated with water at pressures up to 20 atmospheres At ordinary temperatures only traces of extract were obtained, at 5 and 10 atmospheres 1 38 and 13 5 per cent were obtained, while at 20 atmospheres the cellulose was completely transformed into a jelly like mass which could be powdered when dry and had, apparently, the empirical composition $C_{12}H_{22}O_{11}$

When cotton yarn is boiled with water for a long time it shrinks and loses tensile strength The following experiments, made by the authors may be quoted

Twenty leas of cotton yarn were boiled with water for three hours, dried, and remeasured, under similar atmospheric conditions This was repeated on successive days till no further shrinkage could be observed The figures obtained were–

	Loss in Length per Lea Average of 20 Tests
After first boiling	37 5 inches
" second boiling	29 0 "
" third "	17 0 "
" fourth "	0 0 "

This corresponds to a shrinkage of about 2 per cent The tensile strength of the yarn decreased from 26 5 lbs to 25 25 lbs

Steaming unbleached cotton yarn produces an increased colour, and improves its appearance also The thread becomes softer and the curled places disappear entirely (*J Text Inst*, 1923, T 81) It was suggested (*loc cit*) that American yarn can be steamed to produce the appearance of Egyptian yarn To effect the maximum improvement in appearance with the minimum development of colour, it was proposed to subject yarn to the action of steam at 7½ lbs. pressure

for times varying from ten to thirty minutes, according to the type. Soaking in cold water for a week, or in hot water for a shorter period, makes cotton yarns more uniform in twist and strength, while schreinerising depends upon the swelling of the fibre in water at elevated temperatures.

The moisture content of cotton goods has an important influence on some of the physical properties, such as tensile strength and plasticity These will be dealt with elsewhere

The electrification of cotton is the source of trouble, and its effects are most pronounced in spinning. Electrical effects are related closely to the humidity of the atmosphere, and it is a matter of common experience that the air must contain an adequate amount of moisture if trouble is to be avoided

Slater (*J Text Inst*, 1925, P 59), as the result of exhaustive experiments, has arrived at the following conclusions —

1 The electrical conductivity of cotton, or the rate at which intense local charges in cotton can be dissipated, is increased when either the relative humidity or the temperature (or both) is raised.

2 The relative humidity is the more important factor in the control of electrification

3 Over ranges of relative humidities and temperatures obtaining in spinning practice, (*a*) the electrical conductivity doubles its magnitude for every 4·0 per cent rise in relative humidity, and this is approximately the same for all cottons, (*b*) the electrical conductivity doubles its magnitude when the temperature is raised approximately 16° F. This is not a constant for all cottons

4 For temperatures obtaining in practice, it is desirable that the relative humidity should not fall much below 40 per cent if electrification is to be avoided Between 55 and 60 per cent is a convenient relative humidity

5 For each per cent of relative humidity there are two equilibrium values of the conductivity, depending on whether the cotton has been previously exposed to an atmosphere of higher or lower relative humidity The value when approaching from wetter conditions is several times greater than after approaching from drier conditions

6. It is always more difficult to raise the conductivity of the cotton to a critical value, by raising the relative humidity, than to lower the conductivity from a critical value, by allowing the relative humidity to fall

The Action of Acids.—In general terms, it may be stated that strong acids cause rapid tendering of cotton, the rate and amount depending upon the temperature and concentration Weak acids have a less destructive action depending upon their hydrogen-ion concentration There are two kinds of tendering by acids In the absence of air the action is one of hydrolysis, resulting, as explained above, in the formation of hydrocellulose If, however, air or an oxidising agent be present, oxycellulose is also formed Further, certain acids, such as nitric and acetic, are capable of forming ethereal salts of cellulose, while concentrated solutions of strong mineral acids produce an initial effect very similar to that of mercerisation.

Action of Sulphuric Acid.—Cold concentrated sulphuric acid dissolves cotton, and if the solution produced be poured quickly into excess of cold water, the cellulose is reprecipitated in a gelatinous condition termed "amyloid" This consists probably of hydrated cellulose, $(C_6H_{10}O_5)_2H_2O$ If the sulphuric acid solution be allowed to stand for some time, no precipitate is produced on dilution, owing to the complete hydrolysis of the cellulose to dextrose If the sulphuric acid solution be warmed, rapid decomposition sets in, accompanied by charring and the evolution of carbon dioxide and sulphur dioxide. The

reaction with cold concentrated sulphuric acid is employed in the manufacture of parchment paper Sheets of unglazed paper are immersed in sulphuric acid of about 78 per cent strength, and then in cold water to precipitate the gelatinous amyloid on the surface The treated paper is then washed with water till free from acids and dried

Sulphuric acid of a somewhat less concentration acts differently When cotton hairs are immersed in acid of about 105° Tw (62 per cent) strength they untwist rapidly, and at the same time swell up and become shorter When cotton yarn is treated in this way it not only shrinks but acquires an increased tensile strength and affinity for direct dyestuffs These effects are similar to those produced by mercerisation The immersion in acid must not be prolonged or the cotton will be gradually dissolved or tendered

The action of mineral acids of moderate concentration, and especially of sulphuric acid, on cotton, has formed the subject of many patents for the production of wool like and transparent effects These are due chiefly to Heberlein According to Eng Pat 10867A, 1917 (*J S C I*, 1918, 297A), increased transparency is obtained by treating the material with a solution of caustic soda of sp gr 1 15 at temperatures below 0° C, followed by treatment with sulphuric acid of sp gr 1 50 also below 0° C The treatment may be repeated till the desired effect is obtained Wool like effects are claimed to be obtained (*J S C I*, 1923, 180A) by subjecting cotton fabrics to the action of concentrated sulphuric acid of sp gr 1 515 to 1 546, and, after washing, treating with caustic soda solution without tension Similar effects are obtained by treatment with nitric acid (sp gr 1 424 1 468), or (1) a solution of zinc chloride of 1 842 sp gr, (2) hydrochloric acid (3) Schweitzer solution or other cellulose solvent

Heberlein states, also that linen like effects are obtained when cotton is subjected to one treatment with caustic soda solution of specific gravity of not less than 1 116, and one treatment with concentrated sulphuric acid.

In a later patent (Eng Pat 196298, 14th April 1923) it is claimed that this action of concentrated sulphuric acid is modified considerably by the presence of a heterocyclic base such as pyridine or quinoline In the presence of these bodies the time of action can be prolonged considerably without causing hydrolysis of the cellulose

For example, bleached mercerised muslin is rendered transparent and soft by treatment for four minutes with a mixture of 1 pint of pyridine and 4 pints of sulphuric acid of 66° Bé (sp gr 1 84), and a wool like effect is produced on suitable mercerised cotton fabric by treating it with a mixture of 1 pint of pyridine and 9 pints of sulphuric acid of 55 5° Bé (sp gr 1 66) for five minutes The linen like effects on cotton obtained by the methods described in Eng Pat 192227 (*J S C I*, 1923 306A) may be produced by means of simple treatment of cotton with a mixture of sulphuric acid and a heterocyclic base

Kashitani (Eng Pat 144083, 28th May 1919) uses the following process

Cotton yarn or fabric is treated for one to fifty minutes in sulphuric acid of 52° to 60 Bé (sp gr 1 56 1 71), washed in water under vibration to remove loose fibre, immersed for ten to fifteen minutes in a solution of caustic soda of 8° to 15° Bé (sp gr 1 06 1 12) to improve the lustre, neutralise the free acid, and maintain the colour, then treated with a 3 per cent solution of borax to render it non combustible and neutral The fabric may be further softened by treatment with a 5 per cent solution of glycerin, or with calcium chloride, glucose, or soap solution

Cold dilute solutions of sulphuric acid do not tender cotton, provided that the acid is subsequently washed out completely, before the cotton is allowed to

dry. But some of the acid is adsorbed. This was studied by Leighton (*J S C.I.*, 1916, p. 464) in the following manner:—

About 1 gramme of purified cotton was shaken for three hours with 100 c.c. of aqueous acid of varying concentrations, then centrifuged for one hour, and the acid retained by the cotton determined. The liquid separated from the cotton was also titrated. It was found that hydrochloric, sulphuric, and phosphoric acids do not form compounds with cellulose at ordinary temperatures. Cellulose adsorbs sulphuric acid more than phosphoric acid, and the latter more than hydrochloric acid, whilst the presence of any of these acids reduces the amount of water which can be adsorbed by cotton; differences in the results obtained by titration of the residual solutions, and gravimetric determination of the acid retained by the cotton, are due to the former method, giving only the selective adsorption of the acid Selective adsorption does not occur with phosphoric acid, and is more pronounced with hydrochloric than with sulphuric acid. Selective adsorption was only pronounced at high concentrations of the acids.

When cotton is boiled with a dilute solution of sulphuric acid it loses tensile strength rapidly, owing to the formation of hydrocellulose. But a diminution in tensile strength is observed before the presence of hydrocellulose can be detected.

If heated with acid under pressure hydrolysis becomes extremely rapid. Even traces of sulphuric acid are sufficient to convert cotton into a mass of hydrocellulose at a temperature of from 130° to 140° C. The treated cotton retains its original structure, but, when washed and dried, breaks down rapidly into a powder, consisting of hydrocellulose.

When dilute sulphuric acid is allowed to dry into cotton, its tendering action is greatly increased. Knecht and Thompson (*J. Soc. Dyers and Col*, 1921, p 270) indicate two reactions, viz (1) partial hydrolysis accompanied by reduction of tensile strength, and (2) the fixation of some acid in the fibre which acts as a mordant for basic dyestuffs The drying in of acid is accompanied, also, by oxidation which produces oxycellulose They distinguished between two kinds of acid damage, according to whether it is produced by prolonged action of weak acid with or without drying (p 117).

When cotton is boiled for half an hour with a 0 5 per cent. solution of sulphuric acid, its tensile strength becomes less, although no hydrocellulose is formed. That is, the prolonged action of dilute acids, unaccompanied by drying, produces no chemical change. When dilute sulphuric acid is dried into cotton, not only is hydrocellulose produced, but at the same time some of the sulphuric acid becomes fixed and cannot be washed out by either water or alkali. It is this fixed sulphuric acid which, according to Knecht and Thompson, gives the cotton an increased affinity for basic dyestuffs

Lawrence (*J S.C I*, 1919, 894A) found that the tendering action of dilute sulphuric acid on cotton yarn depends on (1) the concentration of the acid, and (2) the temperature of drying He gives the following example. Cotton yarn, after treatment with N/100 sulphuric acid, was dried at various temperatures and the tensile strength tested. When dried at 20° C the loss was 2 per cent., while at 100° C. it was 67 per cent Acid of N/5 strength caused a loss of 67 per cent. at 20° C. Lester (*J S.C I*, 1915, p 934) concluded that less than 0·1 per cent of acid will produce tenderness under normal conditions when dried into cotton, while if the goods are ironed or stored, as little as one part in ten thousand is quite sufficient to cause damage But in a recent patent, it is claimed that cotton, treated with from 0·1 to 0·2 per cent of sulphuric acid, or an acid sulphate, and dried at a low temperature, actually has an increased

tensile strength of from 20 to 30 per cent., and that only traces of hydrocellulose are formed

Hydrochloric acid acts in a similar manner to sulphuric acid, but is more destructive in its effects, owing to its greater hydrogen-ion concentration Dry hydrochloric acid gas converts cotton into a friable mass of hydrocellulose, and if dissolved in carbon tetrachloride causes carbonisation Willstätter (*J.S C I.*, 1913, p 822) observed that cotton is completely dissolved by cold hydrochloric acid of 1 209 specific gravity (or 40 per cent.). Ordinary commercial hydrochloric acid does not dissolve cotton. Solutions containing from 37 to 38·5 per cent of hydrochloric acid cause it to swell up and become transparent, while at concentrations of from 36 to 37 per cent mercerising effects are produced The greater tendering action of hydrochloric acid compared with that of sulphuric acid was measured by Thompson (*J. Soc Dyers and Col.*, 1915, p. 255), who found that a $\frac{1}{4}\frac{1}{000}$ per cent solution of hydrochloric acid when dried into cotton and heated at a temperature of 20° C for ten minutes caused as much tendering as a $\frac{1}{12}\frac{1}{8}$ per cent solution of sulphuric acid. Similarly, when boiled, the corresponding strengths are $\frac{1}{4}\frac{1}{2}$ per cent for hydrochloric acid and $\frac{1}{12}\frac{1}{8}$ per cent. for sulphuric acid Similar results were obtained by Fort and Pickles (*J Soc Dyers and Col*, 1915, p 255), who determined the loss of tensile strength produced by different acids of the same concentration Thus, after boiling cotton for one hour with normal acid the percentage losses were—

Hydrochloric acid	93 5
Sulphuric acid	71 0
Sodium bisulphate	53 0
Acetic acid	10 9

Padding, followed by drying, gave similar results The addition of a similar ion to the acid, which diminishes electrolytic dissociation, causes a diminution of the tendering power The decrease in tendering power of a strong acid when a salt of a weaker acid is added, is due to the liberation of the weaker by the stronger acid, *e.g.*

$$H_2SO_4+CH_3COONa=Na_2SO_4+CH_3COOH$$

The effect of the stronger acid cannot be completely eliminated in this way, since an equilibrium is established, beyond which the reaction does not proceed, or, in other words, the equation is reversible. The same authors (*J S C.I*, 1916, p 38) conclude that the tendering action of acids is proportional to their strength, as indicated by their relative velocities of inversion of cane sugar In the case of salt solutions, and mixtures of salts with acids, the degree of tendering is governed by the laws of electrolytic dissociation.

Coward, Wood, and Barrett (*J. Text. Inst*, 1923, T 520) have also compared the tendering action of various acids in the following manner. Air-dry samples of bleached cotton fabric were immersed for one, fifteen, and sixty minutes respectively in 2N, N/1, N/10 solutions of the following acids. Hydrochloric, sulphuric, hydrofluoric, acetic, monochloracetic, and trichloracetic The immersions were made at temperatures of 100° C., 60° C , and 40° C., and the resulting losses in tensile strength determined after washing the fabric in cold water and drying by exposure to air. They found that the amount of tendering, for a given acid, depends upon (*a*) the concentration of the acid, (*b*) the time of action, and (*c*) the temperature. For the same temperature, the loss of strength was roughly proportional to the hydrogen-ion concentrations. With normal sulphuric acid and hydrochloric acid, complete tendering was produced in fifteen minutes, and even with N/10 hydrochloric acid a similar result was obtained. Measurable

tendering was observed when a fabric containing its own weight of a 0·01 per cent. solution of hydrochloric acid was dried into the cotton at a temperature of 100° C for one hour, while with a 0·05 per cent solution the tendering was much more marked The action of hydrochloric acid when dissolved in non-aqueous solvents, alcohol, ether, and benzene, was investigated. These solutions all had markedly stronger tendering effects than solutions of the same concentrations in water at the same temperature Dry gaseous hydrochloric acid acted very slowly on dry cotton at the laboratory temperature, producing less than 20 per cent. of loss of tensile strength after two hours' exposure at 15° C., but, in the presence of a little moisture, tendering became almost instantaneous under the same conditions The measurement of the viscosity of cuprammonium solutions of cotton fabrics was found to give more sensitive indications of damage produced by acid than the determination of tensile strength (*q v*)

Acid salts, or salts which, like aluminium sulphate, have an acid reaction in aqueous solution, also tender cotton. Those like magnesium chloride, which are decomposed on drying, are particularly destructive The action of these salts is explained by the equations

$$2NaHSO_4=H_2SO_4+NaSO_4,$$
$$Al_2(SO_4)_3+2H_2O=Al_2(SO_4)_2(OH)_2+H_2SO_4,$$
$$Al_2Cl_6+2H_2O=Al_2Cl_4(OH)_2+2HCl,$$
$$MgCl_2+H_2O=Mg(OH)Cl+HCl,$$
$$ZnCl_2+H_2O=Zn(OH)Cl+HCl$$

The tendering action of these salts is, also, reduced by the presence of sodium salts of the same or of a weaker acid. Zinc chloride and magnesium chloride, which are used in sizing mixtures, are not uncommon causes of tendering, especially when the goods are singed or ironed Thomson (*J Soc Dyers and Col*, 1915, p 133) states that although the chlorides of magnesium and zinc tender cotton when used separately, yet together they have hardly any action, owing, probably, to the formation of a relatively stable double chloride The tendering action of certain metallic chlorides was measured by Fox, Hubner, and Knecht (*J S C I*, 1912, p 810), who give the following figures —

Salt	Percentage Loss of Tensile Strength		
	After Sizing three Times.	After Boiling	Total
Ammonium chloride	5 5	26 0	31 5
Calcium chloride	11 0	10 0	21 0
Magnesium chloride	6 0	17 0	23 0
Sodium chloride	12 5	10 0	26 0
Zinc chloride	3 0	29 0	26 0
Aluminium chloride	22 0	23 0	45 0

The action of sodium chloride, a neutral salt, and the initial effect of zinc chloride, are both of interest

Organic acids do not attack cotton so readily as mineral acids. The volatile acids, such as formic and acetic acids, are, moreover, largely expelled when cotton containing them is dried. Organic acids which, like oxalic acid,

are not volatile have a tendering effect proportional to their hydrogen-ion concentrations. The tendering action of an organic acid is increased on drying in presence of the sodium salt of a stronger acid. This is due to a slight reversion of the equation

$$H_2SO_4 + 2CH_3COONa \rightleftharpoons Na_2SO_4 + 2CH_3COONa.$$

Occasionally, one meets with cases of tendering which can only be explained in this way Such finishing processes as calendering would accelerate the action But Fort and Pickles (*loc cit*) found that oxalic acid did not act in this way, its tendering effect being diminished by the addition of sodium sulphate They explain this as being due to diminished electrolytic dissociation owing to the formation of acid salts of the dibasic acid

If cotton be boiled with solutions of organic acids a distinct loss of tensile strength is produced. This is of importance in the dyeing of wool and cotton mixtures in an acid dye bath, in which formic or acetic acid is generally substituted for sulphuric acid

Zanker and Mann (*J S C I*, 1917, p 708) state that tensile strength tests of cotton boiled with water, acetic and formic acids, under conditions the same as those used in dyeing wool and cotton mixtures, showed a loss of strength of 40 to 50 per cent for acetic acid and 50 to 55 per cent for formic acid. They note, further, that acetic acid cannot be washed out of cotton completely except by passing steam over it at a temperature of 200° C Cotton has the power of adsorbing a considerable amount of tannic acid from its aqueous solution. This property is made use of in mordanting cotton for dyeing with basic dyes No tendering is produced In the experiments quoted above, the addition of sodium sulphate produced, apparently, a somewhat different result For cotton alone the loss of tensile strength was reduced to about 25 per cent When, however, wool was present with the cotton the loss of strength became increased to from 50 to 55 per cent for acetic acid and 30 to 60 per cent for formic acid If a strong solution of oxalic acid, thickened with gum, be allowed to dry into cotton no tendering takes place, but the material has an increased affinity for basic dyes and a decreased affinity for direct colours Knecht has shown that this is due to the formation of a cellulose formate owing to the decomposition of the oxalic acid on drying into formic and carbonic acids If the cotton be boiled with alkali to decompose this cellulose formate the increased affinity for dyes is lost again The organic acids, under suitable conditions, have another important action on cotton cellulose They form ethereal salts, such as acetates and formates When cotton is heated with acetic anhydride under pressure an acetate of cellulose is produced The composition of the acetate depends upon the proportion of acetic anhydride used, the temperature of the reaction, and the presence or absence of a hydrolysing agent such as zinc chloride, from one to five acetyl groups being introduced. The more important acetates are · Triacetate, $C_6H_7O_2(C_2H_3O_2)_3$; tetra-acetate, $C_6H_6O(C_2H_3O_2)_4$, penta-acetate, $C_6H_5(C_2H_3O_2)_5$. The formation of cellulose penta-acetate is shown by the equation

$$C_6H_{10}O_5 + 5CH_3COOH = C_6H_5(CH_3COO)_5 + 5H_2O.$$

The cellulose acetates are insoluble in water but dissolve in glacial acetic acid and various organic solvents When a solution is evaporated a clear insoluble film of the acetate is obtained. The solution may be spun into silk by forcing its solution through fine orifices and evaporating the solvent from the issuing viscous thread Cellulose acetate silk is made in this way (p. 167).

The acetates of cellulose have other important properties. They are quite insoluble in water, are bad conductors of electricity, and are non inflammable. On account of these properties they are used largely in the preparation of waterproof dressings, insulating materials, and photographic films Cellulose acetate is decomposed into hydrated cellulose and potassium acetate when boiled with aqueous or alcoholic potassium-hydroxide solution—

$$C_6H_7O_2(C_2H_3O_2)_3 + 3KOH = C_6H_7O_2(OH)_3 + 3C_2H_3O_2K.$$

The Detection of Traces of Mineral Acid.—Though often of importance, this is a matter which presents some difficulty A method which sometimes serves, is to moisten the cotton with hot distilled water and then wrap it round a piece of neutral litmus paper If pressure be now applied, a colour change is produced. Methyl orange may be used as the indicator instead of litmus Briggs tests for free acid in the following manner. To a solution of potassium iodide and iodate in water containing dissolved starch, decinormal acid is added till a light blue colour is produced The mixture is then boiled till it becomes colourless. If cotton be treated with this reagent a blue stain is produced in the presence of free acid The indications of the test have a rough quantitative value depending on the time required to develop the blue colour This appears at once in the presence of an objectionable quantity of acid, while if no sign of a blue colour appears in five minutes the cloth may safely be regarded as neutral. Another method is to boil the goods with distilled water and phenolphthalein and titrate at the boiling-point with centinormal sodium hydroxide. The following table by Coward and Wigley (*J Soc Dyers and Col*, 1922, p 260) gives the limits of delicacy of certain other indicators for spotting tests It will be observed that methyl red is the best to use, being capable of detecting as little as 0·005 per cent of acid or alkali

Indicator	Acid or Alkalinity	Colour
Thymol blue	0 16 per cent H_2SO_4 and upwards	Purple
Methyl orange	0 10-0 16 per cent H_2SO_4	Yellow red
Lacmoid	0 06 per cent H_2SO_4 and upwards	Red
	0 03–0 06 per cent H_2SO_4	Blue centre red ring
	0 02 per cent H_2SO_4 and less	Blue
KI-KIO_3-starch	0 01 ,, and upwards H_2SO_4	Blue
Methyl red	0 005 ,, H_2SO_4 and upwards	Red
	0 005 ,, NaOH and upwards	Yellow
Bromothymol blue	0 02 ,, NaOH (as Na_2CO_3)	Green
	0 04 ,, NaOH and upwards	Blue
Phenolphthalein	0 12 ,, NaOH and upwards	Pink

Free sulphuric acid may be extracted from cotton by means of absolute alcohol, and after evaporation of the spirit either titrated or weighed as barium sulphate.

The same authors state that acid is removed more quickly by a solution of salt in water than by water alone When cotton is washed till it is neutral to methyl red it cannot contain more than 0·005 per cent of hydrochloric acid or its equivalent Both acid and alkali may be estimated by boiling the fabric with water and titrating it with phenolphthalein as indicator, the results being correct within 0·02 per cent.

Action of Nitric Acid.—Owing to its oxidising action, nitric acid does not

react with cotton in quite the same way as hydrochloric or sulphuric acids, oxidised cellulose being produced with or without hydrocellulose. Moreover, it forms esters or cellulose nitrates Cold concentrated acid has a mercerising effect According to Knecht and Lipschitz (*J.S.C.I.*, 1914, p. 117) this action begins only at a strength of 76° Tw, the maximum effect being produced at 83° Tw Cotton soaked in cold nitric acid of these concentrations shrinks, acquires an increased tensile strength, and a greater affinity for basic, direct, and sulphur dyes. The microscopic structure of the cotton is also affected, becoming very similar to that of mercerised cotton The action of the nitric acid is very rapid, being complete in about five minutes If the nitric acid be washed out under tension to prevent shrinkage, the cotton acquires also a silky lustre The authors consider that the first action of the nitric acid is to form the nitrate $C_6H_{10}O_5HNO_3$ which is decomposed by washing into cellulose and nitric acid Prolonged action for from four to six hours gives a stable nitrate, the nitrogen content of which increases up to a maximum, and then by continued contact with the nitric acid diminishes to a negligible quantity The extent of the action depends upon the concentration, temperature, and time of action of the nitric acid With constant concentration, the time required to produce a given result is shortened by increasing the temperature Thus with acid of 83° Tw the maximum amount of firmly combined acid was obtained in three hours at 31° C Raising the temperature to 61° C. caused the expulsion of all the nitric with the formation of oxycellulose At concentrations below 76° Tw no mercerisation is produced but simply oxycellulose Cold concentrated nitric acid decomposes cotton completely with the formation of oxycellulose and simpler compounds, such as oxalic acid The action is of course much more rapid at higher temperatures. When cotton is boiled with moderately dilute nitric acid, *e g* 50 per cent, it is first changed into oxycellulose, which on prolonged boiling breaks down, gradually forming oxalic acid Even very dilute solutions gradually produce the same result accompanied by rapid loss of tensile strength

Haeussermann describes the action of nitric acid as follows: With cold acid adsorption takes place first, but if contact be prolonged esters are formed, with acid of specific gravity of 1·36 The rate of esterification rises rapidly with the increase in concentration of the acid, and is very marked at specific gravity 1·45 The following details are given —

Specific Gravity of Acid	Action.
1 469 1 476	Dissolves cotton immediately The products are precipitated by water
1 45	Dissolves cotton when warmed, giving first of all nitrocellulose
1 3	Oxidises cotton on the water bath, giving oxycellulose and soluble products
1 2	Disintegrates cotton, yielding soluble products

Many patents have been applied for with the object of producing wool-like effects on cotton based upon the above facts They consist generally of soaking the cotton in cold nitric acid of from 65 to 75 per cent. strength for periods varying from a few minutes to half an hour and then washing with water. According to the process of Gillet et Fils (*J.S.C.I.*, 1920, 654A), wool-like characteristics can be imparted to vegetable fibres by simple immersion in nitric acid (65 to 75 per cent) for not more than half an hour, followed by washing with water The fibres may be treated in any stage of their preparation and the temperature should be less than 20° C If nitric acid stronger than

75 per cent. be used, the treatment must be carried out more quickly. Print effects may be produced directly or by means of reserves. The fibres so treated increase in weight.

In another method (*J.S.C.I.*, 1920, 542A) it is claimed that cellulose fibres coated with nitrated starch compounds have wool-like properties, are strong and soft, and dye directly with basic dyes. The fabric is treated for several minutes at 5° to 20° C with a solution of starch in 65 per cent. nitric acid, then preferably treated with a solution of any suitable salt to aid the precipitation of the nitrated amylaceous substance, and afterwards washed Alternatively the fabric may be first dressed with a starch paste, dried, treated with 65 per cent. nitric acid, the excess acid expressed, and washed Print effects may be produced with the nitrated starch

Cold dilute nitric acid has no action on cotton, but if allowed to dry a mixture of hydrocellulose and oxycellulose is produced When cotton is treated with a cold mixture of concentrated nitric and sulphuric acid, cellulose nitrates (or nitrocellulose) are formed.. Many nitrates have been described, the product varying with the conditions of the reaction The most important are the tri- and tetra-nitrates, the formation of which is represented by the equations

$$C_6H_{10}O_5+3HNO_3=C_6H_7O_2(NO_3)_3+3H_2O,$$
$$C_6H_{10}O_5+4HNO_3=C_6H_6O_2(NO_3)_4+4H_2O.$$

Nitrocellulose silk, colloidon, celluloid are prepared from mixtures of the tri- and tetra-nitrates Gun cotton is also nitrocellulose The tri- and tetra-nitrates dissolve readily in a mixture of alcohol and ether and in other organic solvents. The solution in alcohol and ether constitutes colloidon, while combined with camphor the residue after removing the solvent is celluloid Artificial silks such as Chardonnet, Lehner, and Du Vivier are all derived from nitrocellulose (p 162) Nitrates of cellulose are decomposed when heated with sodium or potassium hydroxide with the formation of the nitrate of the metal and cellulose —

$$C_6H_7O_2(NO_3)_3+3KOH=C_6H_7O_2(OH)_3+3KNO_3.$$

The Action of Alkalis.—While acids " tender " cotton, alkalis, except under certain conditions, do not Mild alkalis, such as borax or sodium carbonate, have no deleterious action, in the absence of air, either in cold or boiling solutions. In the presence of oxygen their prolonged action, at high temperatures, may produce oxycellulose and tendering Dilute solutions of strong alkalis act in the same way as mild alkalis In the absence of air, cotton may be heated, under pressure, with a dilute solution of sodium hydroxide (*e.g* 2 per cent) for some hours without becoming tendered. But if air be present, and particularly in the presence of an oxygen carrier, such as iron or copper oxide, oxycellulose is produced. This can be demonstrated readily by boiling cotton in a dilute solution of sodium hydroxide containing a little manganese chloride and passing a stream of air through the boiling liquid. If cotton yarn be used for the experiment, it will be found to lose its tensile strength very rapidly and to give the reactions for oxycellulose.

Cotton has the power of adsorbing sodium hydroxide from its solutions. It is a matter of common knowledge that, after boiling cotton with caustic soda solution as in bleaching, much washing is required to remove the last traces of the alkali If cotton be soaked in a solution of sodium hydroxide, the concentration of the solution is found to diminish These facts indicate that some of the sodium hydroxide has been withdrawn from the solution with the formation of an unstable compound which is commonly termed alkali cellulose. This

compound was observed first by Mercer, who stated that a definite chemical compound is formed corresponding to the formula $(C_6H_{10}O_5)_2$ 2NaOH which when washed with excess of water breaks down and forms cellulose hydrate $(C_6H_{10}O_5)_2$ H_2O. He observed, further, that when cotton yarn was treated with a cold concentrated solution (20 to 30 per cent) of sodium hydroxide, and subsequently washed with water, certain new properties were developed, viz —

1 It acquired an increased tensile strength
2 A considerable shrinkage occurred
3 It had an increased affinity for direct dyestuffs

These experiments resulted in the development of the process of mercerisation, which will be described later But, apart from mercerisation, the shrinkage produced by cold concentrated solution of sodium hydroxide is made use of for producing general shrinking or local or crepe effects It is also available for the production of a more deeply dyed pattern on a lighter ground of the same colour

The reaction between sodium hydroxide and cotton was studied, further, by Gladstone His method, according to Hubner and Teltscher (*J S C I*, 1909, p. 641), consisted in immersing cotton in sodium-hydroxide solutions of varying concentrations, pressing out the excess of the reagent and washing the residue repeatedly with alcohol The washed cotton was then dried in a vacuum and the combined sodium hydroxide determined from the increase in weight, or by washing it out with water and converting it into sodium sulphate, which was then weighed From these experiments Gladstone concluded that only a portion of the sodium hydroxide could be removed with alcohol, the residual compound having the formula $(C_6H_{10}O_5)_2$ NaOH This was resolved by water into cellulose hydrate, $(C_6H_{10}O_5)_2H_2O$ Gladstone's work, which is of historic interest, has been the subject of much discussion and experiment

Hubner and Pope (*J S C I*, 1904, p 404) concluded, from measurements of shrinkage and affinity for dyes, that cotton yarns adsorb sodium hydroxide, in rapidly increasing amounts, from solutions of from 20° to 26° Tw The adsorption increases more slowly between 26° Tw and 30° Tw, and reaches a maximum at 45° Tw. These authors found that—

1. Cold caustic soda of 1° Tw has a considerable effect in increasing the affinity of cotton for direct dyestuffs, and from 0° to 18° Tw the increase in affinity for the dyestuff is roughly proportional to the concentration of the soda used in the previous treatment of the cotton

2. Between 18° and 22° Tw. the increase in concentration of the soda has a greater effect in increasing the affinity of the cotton for dyestuffs than a corresponding increase of concentration of soda of lower strength

3. The effect referred to in (2) becomes greater with soda of density 22° to 26° Tw, and much greater still with soda of from 26° to 30° Tw

4. Above 30° Tw, however, an increase in strength of the soda exerts a less effect than before in increasing the affinity of the cotton for the colour, so that raising the strength of the soda solution from 30° to 40° Tw. has only about the same effect in increasing the affinity of the fibre for colour as increasing the concentration of the soda from 26° to 28° Tw. or from 28° to 30° Tw. At above 45° Tw increased concentration of the soda produces but little effect in heightening the shade produced on dyeing, so that practically the maximum increase in affinity for colour is got by treating with soda of any concentration between 55° Tw. and 70° Tw, and an experienced eye is needed to see that the dyeing on the hank treated with 70° Tw. soda is stronger than that on the hank treated with 55° Tw. soda.

5 As the concentration of soda used in mercerising is increased above 70° Tw , an actual diminution in the affinity of the fibre for the dyestuff accompanies the increase in concentration , thus, the hank treated with soda of 70° Tw. dyes much more strongly than does that treated with 80° Tw. lye This reversal of the action of the soda is of so strongly marked a character that the hank treated with soda of 80° Tw dyes to the same shade as that treated with soda of 35° Tw.

Another interesting fact, observed by Pope and Hubner, is that while so dilute a solution of sodium hydroxide as 2 per cent distinctly increases the affinity of cotton for direct dyes when used cold, yet if cotton be boiled with it, no increase can be detected The shrinkage was measured also by Pope and Hubner They found that with concentrations of sodium hydroxide of 1° Tw it was appreciably greater than that produced by water alone It increases fairly uniformly up to a concentration of about 18° or 20° Tw , whilst at 20° Tw. a sudden increase in the amount of shrinkage effected is observed to occur. Above 20° Tw the shrinkage increases with the concentration more rapidly than before, the greatest effect being obtained at 45° Tw. As the concentration increases above 45° Tw. the shrinkage observed diminishes continuously until the concentration of 80° Tw. is reached. It will be noted that the maximum shrinkage and affinity for dyestuffs are both developed together These experiments seem to indicate the formation of definite compounds of cellulose and alkali.

Vieweg (*J S C I* , 1907, p 1157) arrived at similar conclusions using a different method He used solutions of sodium hydroxide of accurately determined strength After allowing the cotton to soak in these, the concentration of the solution was determined again by titration and the percentage of alkali adsorbed by the cotton calculated from the difference between the titrations The curve expressing the percentages of sodium hydroxide taken up by the cotton shows two horizontal portions in its rise corresponding to points where further increase in the concentration cause no increase in the percentage taken up by the cellulose The first of these two horizontal portions begins at a concentration of 16 grammes of sodium hydroxide per 100 c.c and extends to 24 grammes per 100 c c It corresponds to a removal of 13 per cent of sodium hydroxide on the cellulose, *i e* to a molecular ratio expressed by the formula $(C_6H_{10}O_5)_2$ NaOH. The second horizontal portion begins at a concentration of 35 grammes per 100 c c It corresponds with an adsorption of 24 per cent of sodium hydroxide or with the formula $(C_6H_{10}O_5)_2$ 2NaOH. Vieweg suggested that alkali cellulose is a definite chemical compound of the composition $C_{12}H_{19}O_{10}Na$, which is capable of combining with more sodium hydroxide until the compound $C_{12}H_{19}O_{10}Na$ NaOH is produced But in another paper (*J S C I* , 1907, p 836) he proposes the formula $(C_6H_{10}O_5)_n$ NaOH, the factor n varying according to the concentration of the alkali, becoming smaller with increasing and greater with decreasing concentrations Under the most favourable conditions for mercerisation n becomes unity

But, on the other hand, Hübner and Teltscher (*J.S C.I* , 1909, p 641) arrived at different conclusions, by repeating Gladstone's experiments under more accurate conditions They found that by very thorough and continuous washing with alcohol, almost the whole of the sodium hydroxide could be removed from cotton, after treatment with solutions of from 1° to 20° Tw With concentrations above 20° Tw the alkali-cellulose compound is more resistant to the action of alcohol Between 23° and 26° Tw. the adsorption of sodium hydroxide rises rapidly, and thereafter slowly to a maximum at 40° Tw. But in all cases sufficiently prolonged washing with alcohol removed nearly all of the alkali. After washing with alcohol till no trace of alkalinity could be

detected in the cotton, it was ashed and the sodium in the ash estimated as sodium sulphate. The authors concluded that the distinct alkali-cellulose compounds described by Gladstone and Vieweg do not exist. Their results are illustrated by the following graph The washing curve (fig. 44) indicates the number of changes of alcohol required to free each sample from sodium hydroxide

Rassow and Wadewitz (*J S C I.*, 1924, 289B) arrived at the conclusion that alkali cellulose is a definite compound of the formula $C_6H_{10}O_5.NaOH$. When cellulose is treated with 18 to 20 per cent sodium-hydroxide solution and the excess pressed out, the remainder of the free alkali can be washed out with absolute alcohol till a stage is reached when the alkali is only removed at a slow but constant rate by "alcoholysis" of the compound $C_6H_{10}O_5$ NaOH Ultimately the whole of the alkali can be removed, leaving regenerated cellulose, which explains the results of Hubner and Teltscher Experiments made with solutions of sodium hydroxide of concentrations of from 10 to 40 per cent indicated an equilibrium between cellulose, alkali, alkali cellulose, and water.

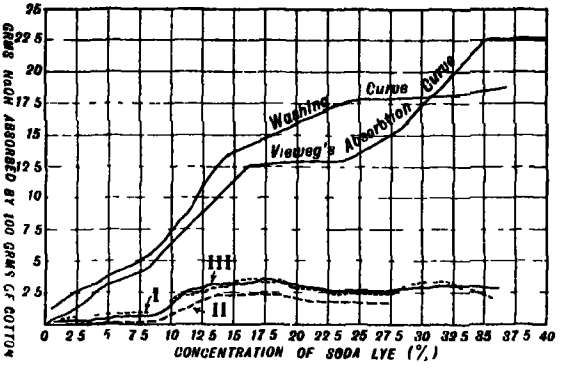


FIG 44

With 35 per cent of alkali, conversion into $C_6H_{10}O_5$ NaOH is practically complete The compound is not formed by the action of sodium ethoxide in alcoholic solution, nor by the action of sodium on cellulose (*vide* Vieweg above)

Dorr (*J Soc Dyers and Col.*, 1924, p 17) considers that certain reactions of alkali cellulose, such as the formation of xanthogenates, similar to sodium xanthogenate, show that it is a true alcoholate of the formula $[C_6H_7O_2(ONa)_3]_n$ The formation of xanthogenate is shown in the equation

$$C_2H_5ONa + CS_2 = SC\begin{matrix}SNa\\OC_2H_5\end{matrix}$$

Leighton (*J S C I*, 1916, p 249) criticises adversely the methods of former workers, and from his own experiments concludes that there is no evidence of the formation of any definite compound of alkali with cellulose

"Hubner and Teltscher's experiments are unsatisfactory, because the quantity of soda remaining in the cellulose, after washing with alcohol, is a function of the temperature, their data show nothing in regard to the way in which cotton adsorbs sodium hydroxide from aqueous solution. The method employed by Vieweg (titration of the soda solution before and after contact with the cellulose)

is quite invalid, because the cotton adsorbs water as well as alkali from the solution. In the present experiments absorbent cotton was purified by heating for eighteen hours at 100° C. with a 2 per cent. sodium-hydroxide solution, souring with dilute hydrochloric acid, washing with alcohol and ether, and drying at 115° C. Trials having shown that one hour's contact, as employed by previous investigators, was insufficient to determine equilibrium, portions of 1 to 2 grammes each of cotton were shaken for three hours with 100 c.c. of caustic soda lyes of various strengths. The cotton was then centrifuged in a brass wire basket, 4·5 inches diameter, rotated at 4000 revolutions per minute. The alkali retained was determined gravimetrically, after incineration with sulphuric acid and ammonium carbonate. It is assumed, provisionally, that after centrifuging for one hour, the cotton is freed from all adherent caustic liquor, the error involved by this assumption being left for subsequent determination. In the same experiments the caustic soda solutions were titrated before and after contact; from the two sets of data it was then possible to calculate the adsorption of water as well as of sodium hydroxide. There is no experimental evidence of the formation of any chemical compound of cotton with sodium hydroxide at any stage of concentration, the graphic representation of the results having the form of a perfectly smooth adsorption curve. Some of the results obtained are set forth in the following table."

Solutions, Grammes NaOH per Litre	1 Gramme of Cotton Adsorbed—	
	Water, Grammes	NaOH, Grammes
475	0 82	0 92
350	1 16	0 83
250	1 66	0 70
150	2 68	0 50
100	3 65	0 37
75	4 00	0 30
50	4 00	0 20
25	4 00	0 10

Still more recently, Coward and Spencer (*J. Text. Inst.*, 923, T. 32) have reviewed and supplemented the work of the investigators mentioned already. According to these authors, "Leighton has attempted a direct estimation of the total alkali absorbed, by centrifuging away the excess liquors and determining the alkali remaining in association with the cotton. He did not determine the water content of the mass, but attempted an indirect estimation of it, in which, however, he became involved in an error which vitiated his results."

Coward and Spencer, by means of a special centrifuge capable of 8000 revolutions per minute, claim to have made the first direct determinations of both the water and sodium hydroxide present in the alkali-saturated fibre.

Samples weighing 8·5 grammes (dry) were immersed overnight in 100 c.c. each of solutions of known weight composition. They were then centrifuged for 7·5 minutes at the rate of 7000 revolutions per minute. The temperature of the experiments was from 15° to 18° C. The amounts of sodium hydroxide and water removed from solutions of various compositions were calculated from determinations of the weight of dry cotton, the total centrifuged mass, and of the sodium hydroxide present in it as determined by titration. The original

paper should be consulted for full details, but the following conclusions may be quoted here —

"The amounts of sodium hydroxide and of water absorbed by cotton from aqueous solutions of sodium hydroxide have been determined directly over the whole range of solubility of sodium hydroxide at laboratory temperature, by means of the analysis of centrifuged material The curves for total sodium hydroxide are complex and give no indication of the formation of definite chemical compounds, nor are they of the form commonly found for simple adsorption On the other hand, the preferential absorption of sodium hydroxide by loose fibre and by fabric, is approximately proportional to the concentration of the solution in contact with the cotton, in this case also there is no evidence of the formation of definite compounds, but the form of the curves is not inconsistent with the view that a series of compounds of the general formula $(C_6H_{10}O_5)_m\ (NaOH)_n$ is formed

"The nature of one factor concerned in the absorption becomes clear when the volume of the absorbed substance is calculated It appears that the cotton hairs swell to an increasing extent as the percentage of sodium hydroxide rises, up to a limit swelling equal to nearly three times the original volume This limit is reached at about 14 3 per cent NaOH, and no further swelling occurs in stronger alkali It is concluded that the cuticle of the hair is responsible for this limitation, since the contents of the hair are capable of much greater swelling when unconstrained by cuticle

'When the cotton hairs are not loose, but are present in yarn which has been woven into fabric, similar results are obtained, except that the maximum swelling is then much less, on account of the additional constraint imposed by the fabric as a whole on the individual hairs

"The thesis that there is a general parallelism between the technical results of mercerisation and the swelling deduced from the above experiments has been developed to explain the superior results obtainable in mercerising yarn as compared with cloth, and to show that the difficulty of penetration of cloth by alkali is not the sole cause of incomplete mercerisation in practice In addition, the residual swelling in fibre mercerised and washed has been measured and shown to be closely proportional to the absorption of benzo purpurin 4B as measured by Knecht, and the diminished swelling of such fibres on soaking in water after drying has been correlated with their well known diminished 'affinity' for dyestuffs after drying

Very marked hysteresis in the shrinkage of cotton fibre on replacement of mercerising solutions by weaker solutions has been observed, and the results give a reason for the necessity in technical operations for retaining cloth under tension until almost the whole of the caustic soda has been removed'

Mercerised Cotton.— Although Mercer's observations in 1844 laid the foundations of the process which now bears his name, yet they were not successfully applied till a long time afterwards This was due chiefly to the fact that the increased tensile strength and affinity for dyestuffs, although valuable for certain purposes, did not compensate for the loss of length involved It was not until 1889 that Lowe discovered that the same effects were produced if shrinkage were prevented by carrying out the process under tension Moreover, an additional important property was at the same time imparted to the cotton yarn, namely, a greatly increased lustre This was made use of by Thomas and Prevost in 1895, and the application of the process of mercerisation on a commercial scale dates from this year

The special properties of mercerised cotton are—

1. An increased tensile strength.
2. An increased lustre.
3. An increased affinity for direct dyestuffs.
4. A greater receptivity for mechanical dressing operations
5. A greater reactivity towards chemical solvents and reagents
6. An increased capacity for absorbing water.
7. When carried out without tension a decrease in length
8. An alteration in microscopic structure.

The process can be applied either to cotton yarns or piece goods In the case of the former, only longitudinal tension is required, but with piece goods both lateral and longitudinal tension are necessary The goods are simply impregnated with cold concentrated sodium hydroxide and then washed thoroughly with water under tension It is immaterial whether the tension be applied throughout or only during the washing

The following is a brief description of the process First of all it is essential that the goods should be perfectly permeable To ensure this, they are scoured, even if already bleached, with a boiling solution of soap and sodium carbonate, and then washed and hydro-extracted. Unbleached cotton is not so often mercerised, but when it is, it must be completely scoured first After scouring, the yarn is soaked in a cold solution of sodium hydroxide of from 55° to 65° Tw (sp gr 1 30), generally under tension, at a temperature not exceeding 65° F. If the yarn be thoroughly permeable the action is very rapid, requiring not more than ten to fifteen minutes for completion. It is then squeezed, rinsed with cold water till nearly free from alkali, treated with dilute acetic acid to neutralise the last traces of alkali, and again washed thoroughly with water and dried If scroop be required it is soaked, before drying off, in a 0 5 per cent. solution of acetic or tartaric acid, and squeezed If not scrooped, soaping, before drying, improves the lustre As a general rule goods are mercerised after bleaching but before drying, but the best results are obtained with bleached dry cotton

The condition in which goods are mercerised is determined by circumstances. These are excellently described by Chibbens (*J Text Inst*, 1923, T 225) as follows " There are many factors which help to determine in practice whether a yarn or fabric shall be mercerised in the grey or in the bleached state. On the one hand, since material mercerised in the grey condition receives an alkali boil in a subsequent bleaching process, it is often unnecessary completely to remove the mercerising alkali by thorough washing or by acidification. On the other hand, bleached cotton does not require a preliminary water boil to facilitate the penetration of the mercerising alkali, as is the case with grey cotton, which must therefore be mercerised wet This not only has the effect of diluting the alkali, but also causes a danger of irregularities arising from an accidental local drying between the boiling process and the actual mercerising Bleached material, on the other hand, is usually mercerised dry, and such irregularities are then more easily avoided Much mercerised yarn is used to produce a weaving design on fabric of unmercerised yarn ; such fabrics must be bleached after weaving, and there is thus no object in using a mercerised yarn which has already been bleached The dilute alkaline liquors obtained as washings from grey mercerised material are, however, more difficult to concentrate and to recausticise satisfactorily, since they contain many impurities extracted from the raw cotton and the size. With fabrics of low tensile strength, it is sometimes more expedient to mercerise in the grey state on account of the resulting increase in strength, which facilitates the subsequent manipulation of the fabric in rope form. Finally,

it has been suggested that mercerised cotton, owing to its greater chemical reactivity, may be more liable to 'modifications' in the bleaching process than

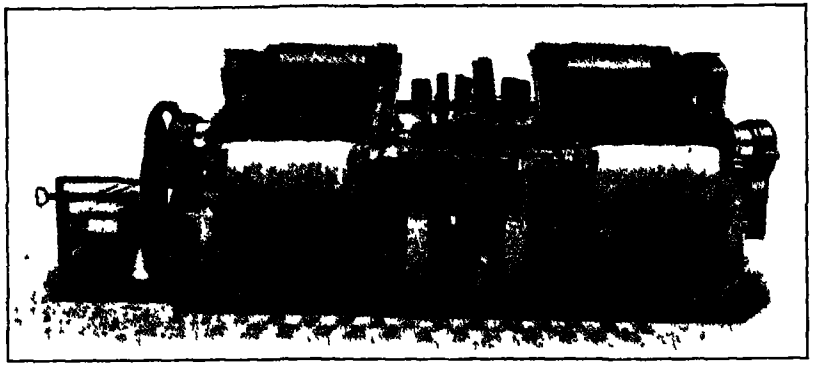


Fig 45.—Hank mercerising machine

unmercerised cotton, and that for this reason material should be bleached before mercerisation. There exists at present no very definite evidence for or against this view. If, on the other hand, an 'oxycellulose' is formed by slight over-bleaching, a subsequent mercerisation results in the dissolution of this oxycellulose by the alkali, and its re-precipitation on the material during washing or acidification; this is known to give a harsh feel to the material. It is sometimes the practice to carry out the alkali kier boil before mercerisation and the hypochlorite treatment after mercerisation."

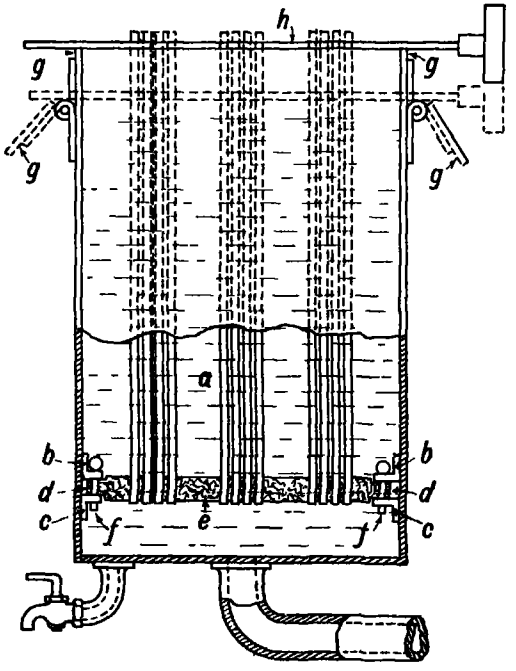


Fig 46.—Friedrich mercerising machine

Cotton yarns are commonly mercerised in the hank form, being impregnated with the sodium hydroxide and washed under tension on a hank mercerising machine.

One by Messrs S. Spencer & Sons is illustrated in fig. 45.

In the Friedrich machine (fig. 46) (Fr. Pat. 424247, 1910, *J S C I*, 1911, p. 742) a rather different mechanism is involved. Along opposite walls and near to the bottom of a rectangular tank, *a* (into which mercerising liquor can be led from a reservoir), are arranged horizontal grooves, *d*, formed by rods, *b*, *c*, placed one above the other, the upper rods being shorter than the lower

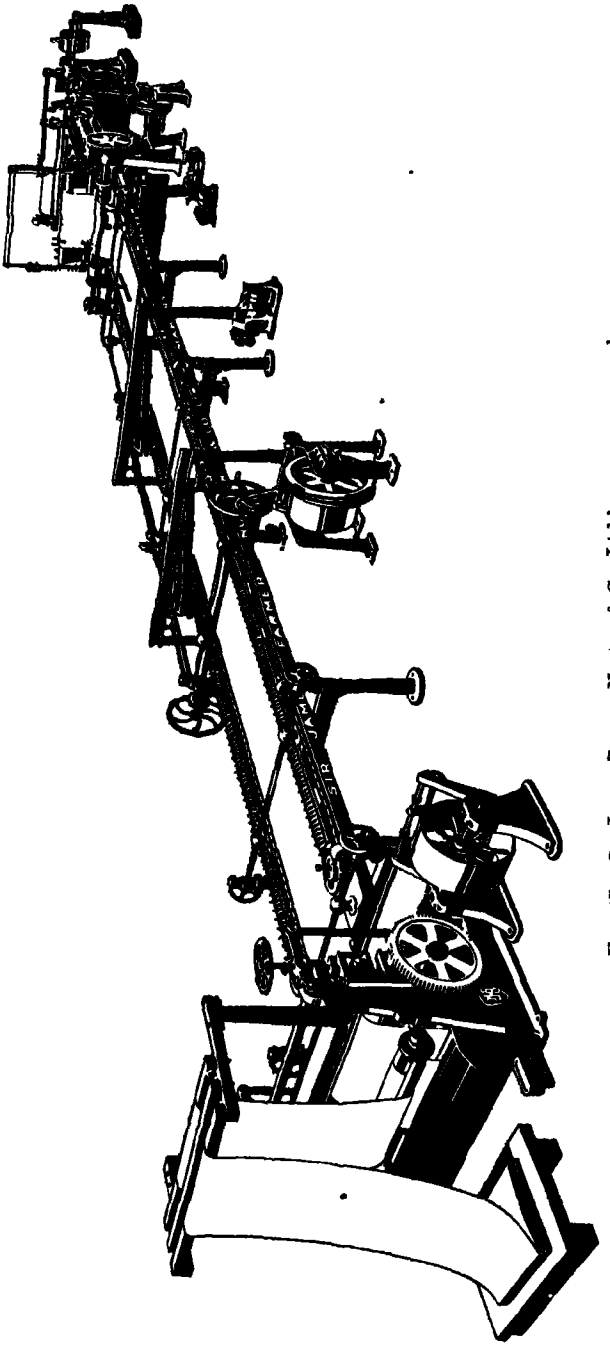


FIG 47.—Sir James Farmer Norton & Co. Ltd 's mercerising machine.

ones so as to permit the ends of the tension rollers, *e*, to be easily introduced into the grooves These rollers are prevented from moving laterally by pegs, *f*. By means of hinged devices, *q*, the height of the walls which support the grooves can be increased so as to subject the yarn hung over the rollers, *h* and *e*, to the required tension during the mercerising process When the hinges, *g*, are turned down, the distance between the rollers, *h* and *e*, is such that the hanks can easily be placed on or withdrawn from them. The upper tension rollers, *h*, are provided with means, *i*, for turning them, and thus keeping the stretched yarn in continuous and reversible motion during the mercerising process

Cotton yarn may be mercerised also by the warp process In this, the yarn is run continuously, in warps, through scouring, impregnating, and washing compartments, being finally wound on drums or bobbins.

Piece goods are, generally, impregnated with the sodium-hydroxide solution in a mangle without tension As soon as impregnation is complete, the cloth

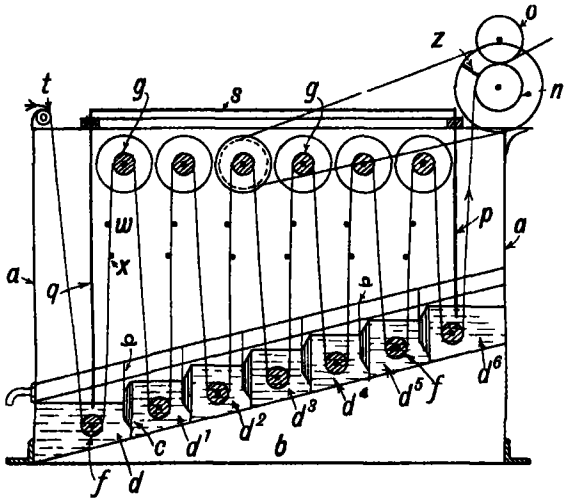


FIG 48 —Matter's mercerising machine

is fed on to a travelling clip stenter which stretches it to its full extent A mercerising machine by Sir James Farmer Norton & Co , Ltd , is shown in fig 47

As the cloth travels down the frame, it is washed by a series of sprinklers Clean water is used for the sprinkler at the farthest end, the washings from this are pumped to the next, and subsequently in rotation to the others. Thus the washings from the sprinkler nearest the impregnating machine are the most concentrated These are treated with calcium hydroxide and, after clarifying and strengthening, used over again After leaving the stenter the cloth is again washed, treated with a dilute acid, and finally washed till free from acid

A different arrangement is shown in fig 48, which illustrates Matter's apparatus (*J.S C I.*, 1908, p 1201) for the impregnation with the lye and its extraction and recovery.

Inside a tank, *a*, is arranged a vessel, *b*, which has an inclined floor and is divided by vertical partitions, *c*, into compartments, *d*, d^1, d^2, etc In these compartments are arranged partitions, *e*, which are slightly removed from the partitions, *c*, and from the floor of the compartments, so that the liquid can fall between two partitions, *c* and *e*, from a higher to a lower compartment. The

machine is also provided with a number of rollers, *g* and *f*, arranged in the higher and lower parts of the machine respectively. Vertical walls, *p*, *q*, provided with a water-sealed cover, *s*, isolate and make air-tight one part of the apparatus, by dipping into the liquid contained in the compartments *d* and d^6. The fabric *t*, coming from the mercerising machine, passes through the apparatus as shown in the figure, and then on to drying cylinders, *n*, *o*. The extraction of the lye from the cloth is effected in the sealed part of the machine. A series of tubes, *v*, arranged transversely in the machine, are so disposed that the cloth comes in contact with them and receives the full force of a steam blast, issuing from perforations in these tubes Shortly after it has left each steam pipe, the cloth passes over a transversely arranged rod, *w*, which expresses the solution produced by the action of the steam on the lye contained in the cloth, and causes it to run down into one of the compartments, *d*, d^1, etc. Before reaching the drying cylinders, *n*, *o*, the cloth is subjected to a jet of water issuing from a pipe, *z* This water subsequently runs down into the compartment d^6, and travels through the apparatus till it reaches the compartment *d*. By regulating the flow of water from the pipe *z*, the strength of the solution which is finally drawn from the apparatus can be adjusted at will.

The following process, dispensing with the use of a stenter, is described by Scheurer, Lauth et Cie (*J S C I*, 1923, 651A), in a sealed note The fabric is impregnated with the caustic soda solution in an ordinary padding machine, being wound on the upper roller of the machine and maintaining it there under pressure so that it cannot shrink In the process of unrolling the fabric is sprayed with, or immersed in, an acid and then wound immediately on an adjacent roller, covered with fabric, which has been mercerised without tension and washed, so that contraction of the acidified fabric is prevented. Since the sodium hydroxide is neutralised instead of being washed away with water it cannot be recovered *The temperature of the reaction* is of importance Clibbens (*J Text. Inst*, 1923, T 224), in a review of the process, states that it appears certain that the effect of temperature upon lustre varies greatly with the concentration of the alkali used With dilute solutions of caustic soda a much better lustre is produced at a low, than at a high, temperature, so that a solution considered ordinarily as being "below mercerising strength" may be made effective by lowering the temperature But for solutions containing 20 to 35 per cent, the effect of temperature is not so marked, and refrigeration of the mercerising liquor can only be useful if dilute solutions containing from 10 to 15 per cent of sodium hydroxide are employed But the patent processes of Heberlein described above should be referred to, in which it is claimed that concentrated solutions of sodium hydroxide at low temperatures produce permanent transparency, especially if followed by treatment with sulphuric acid

Hubner and Pope (*J S C I*, 1904, p 404), who studied the effect of temperature upon lustre with concentrated mercerising solutions, found that the lustre produced at high temperatures (90° C.) was less than that at ordinary temperatures Harrison (*J. Soc Dyers and Col*, 1915, p 198) and Knecht and Harrison (*J. Soc Dyers and Col*, 1912, p. 224) reached the same conclusions. But Clibbens (*loc cit.*) states that the same lustre is produced on yarn with 30 per cent caustic soda at 15° C. and at 90° C., that mercerised at the higher temperature appearing more transparent

Meissner, however (*J Text. Inst.*, 1924, 187A), states that when caustic soda of 53° Tw. is used, temperature has no marked effect and cooling is unnecessary. But more dilute solutions, when cooled to from 0° to 10° C, have a greater mercerising action than solutions of 53° Tw at ordinary atmospheric temperatures.

Barratt and Lewis (*J Text Inst*, 1922, T 17) measured the heat generated when sodium hydroxide acts on cotton. They found that the "heat of mercerisation" increases with the concentration of the caustic soda solution used, though it is not proportional to it When grey or sized cloth is mercerised an appreciable rise of temperature may occur, and hence some system of cooling the liquors to atmospheric temperature is desirable

It is not possible to produce an equally good lustre with every class of yarn As a general rule, hard twisted warps cannot be mercerised On the other hand, the lower the twist the better is the lustre Clibbens states that "the limit is set by the lowest twist which will give sufficient cohesion to the hairs to prevent them from slipping apart under the applied tension. The lustre may therefore, in this sense, be dependent upon the staple length, since the twist necessary to give sufficient cohesion to the hairs, in the case of a yarn spun from long staple cotton, will be less than that necessary in the case of a yarn spun from short staple cotton" A greater lustre is also obtained with double than with single yarns In the case of piece goods a faced cloth, such as sateen, gives the best results when mercerised Willows, Barratt, and Parker (*J S C I*, "Reports on Applied Chemistry," 1922, vol vii p 110) have studied the mercerisation process by treating single hairs with sodium-hydroxide solution under different conditions Their experiments indicate that about three minutes are required for completion of the change At ordinary temperature the axial contraction of the fibre increases rapidly with the concentration of the alkali, till a maximum is reached at a concentration of about 30° Tw. (sp gr 1·15) At 40° Tw (sp gr 1 2) a minimum contraction is observed, while at 50° Tw (sp gr. 1·25) a second flat maximum develops, the contraction approaching zero as the concentration of the alkali reaches 86° Tw. (sp gr. 1·43) The temperature of the treatment is important in determining the concentration at which contraction occurs and its periodical recurrence Well-defined maxima occur at 0°, 18°, 45°, and 85° C The concentrations at which the maxima occur shift with increase of temperature, and at periods beyond each absolute maximum contraction there is a rapid decrease, which at 85° C is most marked and actually becomes an extension It has been mentioned, above, that effects similar to mercerisation can be produced by other reagents than sodium hydroxide Potassium hydroxide is not very effective, more concentrated solutions being required than in the case of caustic soda Mercer found that zinc-chloride solution of a specific gravity of 145° Tw phosphoric acid, and a hot solution of stannous chloride containing three equivalents of water, all had a mercerising action He noted, also, that solutions of sodium hydroxide which are too dilute to produce mercerisation became effective when sufficient zinc hydroxide is added to produce the proportions $Zn(OH)_2$ to 4NaOH

Hubner and Pope (*J S C I*, 1903, p 70) obtained very similar effects with saturated aqueous solutions of potassium iodide and calcium thiocyanate of 1·3 specific gravity, or a solution of the same specific gravity, in which part of the thiocyanate is replaced by calcium chloride, may also be used. The mercerising action of cold hydrochloric acid is peculiar Knecht (*J S C I.*, 1915, p. 134) found that when cotton was soaked in a cold solution of hydrochloric acid of 1·18 specific gravity and then washed it shrinks by about 8 per cent, and acquires an increased affinity for dyes but without any change in microscopic appearance. No increased lustre is produced, however, if the process is carried out under tension.

With regard to the action of zinc chloride, Deeming (*J. Soc Dyers and Col*, 1923, p 306) notes that a 40 per cent solution gelatinises cotton at a moderate

temperature and then dissolves it At a concentration of 50 per cent there is slight untwisting and slow swelling of the hairs, while at 59 per cent., with a temperature of from 65° to 71° C , mercerisation occurs. A 74 per cent. solution gives crepon effects, and a silky lustre when printed on fabrics and dried at 40° to 50° C It is of interest to note that alcoholic solutions of sodium and potassium hydroxides do not mercerise cotton but produce hydrocellulose

The addition of various assistants to the mercerising bath has been patented, sometimes with the object of preventing shrinkage and thus doing away with the necessity for tension, and, at other times, simply to assist penetration of the lye. But decreased shrinkage is always accompanied by decreased lustre Krais (*J S C I.*, 1913, p 19) found the maximum shrinkage to be 31·3 per cent, decreasing with rise of temperature and also in the presence of such bodies as alcohol, dextrin, sodium carbonate, and salts Hence the importance of purity of the lye, since the maximum lustre accompanies maximum shrinkage. It has been mentioned above that the action of sodium hydroxide may be made use of for producing other effects than mercerisation Two examples may be given. Cross and Bevan (Eng. Pat 126174, 1918, *J S C I*, 1919, 458A) have patented the following process for producing hydrated derivatives Fibrous cellulose is treated with caustic soda lye of concentration insufficient to produce mercerisation, *e g.* containing 6 to 11 per cent of sodium hydroxide The treated cellulose is exposed, either simultaneously or subsequently, to the action of carbon bisulphide for six to twelve hours, and is afterwards treated with water. The cellulose fibres are by these means considerably hydrated or swollen to an extent depending on the proportion of alkali to cellulose in the original treatment, and on the temperature at which the alkali was caused to act For example, raw cotton fibre is treated with 2 5 to 3 0 times its weight of caustic soda lye containing 9 per cent of sodium hydroxide and exposed in a closed vessel to the action of 15 per cent of carbon bisulphide calculated on the weight of cellulose The hydration effect is then developed by washing the treated fibre with water, or it may be deferred by washing with brine, the hydration being developed at a later stage by treatment with water In a second patent (*J S C I*, 1919, 759A), cotton textiles or spinner's raw cotton materials are treated with caustic alkali of strength below that which produces the effects of mercerisation, whereby the material is improved in elasticity and extensibility A suitable caustic lye may contain 9 per cent caustic soda, but the strength may be varied somewhat and the treatment carried out between 15° and 50° C.

Cotton which has been "sthenosised," that is, treated with formaldehyde, cannot be mercerised. According to a patent process, cotton is treated with formaldehyde in the presence of ferric chloride, calcium chloride, or alum It is then dried in a vacuum, when trioxymethylene is formed. On stoving the dry cotton, condensation products are formed with the cellulose, which make it resistant to the action of water, alkali, etc The same process may be applied to artificial silk to improve its strength, particularly when wet, or to protect it from damage when cotton is mercerised in its presence. The addition of various other protecting agents, such as alcohols, glycerol, or monoacetin, has been claimed (U S. Pat 1316958, 1919)

The Properties of Mercerised Cotton.—The increased lustre of mercerised cotton will be dealt with in the next section in connection with the microscopic structure With regard to the increased affinity for dyestuffs, it has been noted that this depends directly upon the strength of the caustic soda solution used in mercerisation. Knecht founded a quantitative method of determining the degree of mercerisation upon the estimation of the amount of benzo-purpurin

in which a sample of mercerised cotton will absorb. Pope found that boiling mercerised cotton with water increased its affinity for direct, while decreasing that for basic, dyestuffs The increased tensile strength in the case of individual hairs has been measured by Barratt (*J. Soc. Dyers and Col.*, 1922, p. 117), who uses an apparatus built up from a small Oertling balance

"The right-hand pan of the balance is removed and, in its place, a bundle of steel piano wire is hung vertically with half its length inside a solenoid of covered copper wire, through which an electric current can be sent and accurately measured by means of a sensitive ammeter

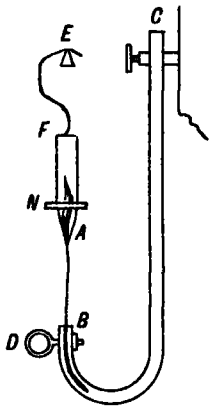
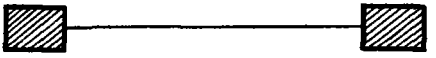


FIG 49.—Barratt's apparatus

"A small weight takes the place of the left-hand pan in order to counterbalance the mass of the magnet on the right An auxiliary knife-edge E (fig 49) is rigidly clamped about half-way along the left arm of the balance, and an easily removable clamp FNA, for holding the end (A) of the fibre to be tested, is suspended from it The other end (B) of the fibre AB is clipped vertically in another adjustable clamp BC, which is attached firmly at C to the central pillar of the balance The fibre, usually of length 13·5 mm., is mounted by means of rubber solution in small double paper squares, as shown in fig 50

"The fibre is first inserted at A, the nut N pushed upwards into position to grip the paper square, and the clamp FNA hung on the knife-edge E The adjustable clamp B of the attachment BC is moved into position vertically below A, and the end (B) then secured firmly by means of the screw D. The balance can then be put in adjustment by lowering the beam supports, so that the smallest possible strain is put on the fibre With the help of the counterbalance it can be so arranged that when no current is passing through the solenoid the pull on the fibre shall not exceed 5 mgm (*i.e.* about $\frac{1}{1000}$th part of the strain that an average cotton fibre will bear without breaking) The pull on the fibre can be increased gradually by passing a current through the solenoid, the magnetised wires being sucked into the solenoid with a force which depends on (*a*)


FIG 50.—Barratt's apparatus

the strength of the magnet (which remains sensibly constant), and (*b*) the amount of current passing through the solenoid (which is accurately measured by an ammeter and controlled by a sliding resistance) This method of applying strain to the fibre avoids sudden jerks A pull is applied gradually and evenly by moving the contact slider, and can be increased or decreased at will and accurately measured at any instant.

"**Calibration of Ammeter.**—This is done by suspending different weights from 0·2 to 15 grammes from the clamp FNA in place of the fibre, the readings of the ammeter being observed when the current through the solenoid is just sufficient to balance these weights.

"**Measurement of Extension of Fibre.**—In order to measure the extension

of the fibre under load, a small rectangular plane mirror was attached in a vertical position to the balance-beam and moved with it as the fibre extended or contracted Another similar mirror, facing the first but inclined at a small angle to it, was firmly secured to a stationary part of the balance. A beam of light incident on the first mirror (M_1, M_1, fig. 51), at a small angle to it, is reflected three times at each mirror, and then passed on to a millimetre scale placed about 150 cm. away.

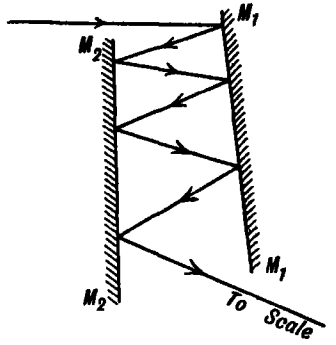


FIG 51 —Barratt's apparatus

"A small angular movement of the mirror M_1, M_1 is sufficient to give a considerable displacement of the spot of light on the scale. In the apparatus used, it was found that an extension or contraction of only 0·0047 cm. of the fibre caused a movement of 1 cm of the spot along the scale, *i.e.* the magnification was over two hundred times (1/0·0047). An exceedingly small elongation or contraction of the fibre can thus not only be observed but also very accurately measured. The scale is placed at such an angle to the beam of light that equal increments of expansion or contraction of the fibre always give very nearly indeed equal amounts of movements of the spots of light "

The results of a number of experiments made with scoured Egyptian fibres were—

	Breaking Strength	Extension as per Cent of Original Length
	Grammes	
Untreated fibres .	7·2	7 4
After mercerisation with caustic soda 45° Tw. . .	6 7	12 2

The results show that mercerised hairs are slightly weaker than unmercerised, but when mercerised without tension their extensibility is over 60 per cent. greater Greenwood (*J Soc Dyers and Col.*, 1920, p 26) found, also, that mercerisation reduced the strength of individual hairs by about 20 per cent. This, together with the increased yarn strength, points to a greatly increased cohesion of the fibres in the yarn, due probably to the removal of the natural wax which would tend to act as a lubricant He gives the following summary of his experiments :—

" From the results obtained, it appears that yarn realises more of the available strength than has been previously assumed. Previous investigators have given 20 to 25 per cent. as the strength realised, as against 67 per cent arrived at by the present author. There are three factors which may account for the difference, viz the number of fibres in the cross-section, the method of testing the yarn strength, and the method of determining the average fibre strength.

" The effect of mercerisation is to increase the strength of the yarn 23 per cent. (without tension), whereas there is no appreciable difference in the individual fibre strength. After mercerising with tension, the yarn again shows an increase in strength ; the individual fibre remains unaltered. This appears to confirm

the previously expressed opinion that the increased yarn strength must be attributed to greater cohesion of the fibres. The swelling and untwisting which occur during mercerisation cause the fibres to bind more closely together.

"Yarn shows an increased strength after bleaching, the increase varying with the previous treatments of the yarn It cannot be concluded, however, from these results that bleaching will always strengthen a yarn, but it can be concluded that bleaching, properly carried out, will not weaken a twofold yarn. The fibre strength, on the other hand, appears to be considerably reduced on an average 20 per cent This, together with the increased yarn strength, points to a greatly increased cohesion of the fibres in the yarn, possibly due to the removal of the natural wax, which would tend to act as a lubricant"

Mercerised cotton absorbs more moisture than ordinary cotton when exposed to moist air. Moreover, according to experiments made by Higgins (*J.S.C I*, 1909, p 188), its capacity for absorbing water increases with the concentration of the caustic soda used in mercerising This is illustrated by the following table —

	Moisture per cent
Ordinary cotton	6 2
Mercerised with caustic soda 10° Tw	6 37
" " " 20° "	6 68
" " " 30° "	8 40
" " " 40° "	9 41
" " " 50° "	9 43
" " " 60° "	9 57
" " " 70° "	9 69

Hubner (*J S C I*, 1908, p 105) observed that mercerised and unmercerised cotton behave quite differently towards a solution of iodine in potassium iodide, the former absorbing much more than the latter He gives the following figures -

Cotton	Ordinary	Mercerised without Tension	Mercerised with Tension
Unbleached	100	154 0	138 8
Bleached	100	145 6	122 2

Not only does mercerised cotton take up more iodine than ordinary cotton, but it retains it much more firmly when washed, especially if zinc-chlor-iodide solution be used Hübner has founded a quantitative method for determining the degree of mercerisation upon these facts (p. 158). Mercerised cotton is dissolved more readily than ordinary cotton by cellulose solvents It is also attacked more quickly by chemical reagents. When boiled with dilute acids, it gives more reducing derivatives, it is more easily oxidised to oxycellulose, and responds more readily to esterification

The hygroscopic nature of mercerised cotton has been referred to above. This has been held to be due to the formation of a hydrated cellulose (or definite hydrate) by the action of the sodium hydroxide followed by washing. Thus, Mercer assigned the formula $(C_6H_{10}O_5)_2.H_2O$ to mercerised cotton. This view

depended upon the fact that mercerised cotton contains, as a rule, more moisture than ordinary cotton under the same conditions, *i.e.* that there is an increase in weight during mercerisation.

Schwalbe (*J.S C.I*, 1909, p. 216) emphasised the difference between hydrolysis and hydration, and that cellulose hydrates may be produced without previous hydrolysis He states that the hydrated celluloses, although differing widely in their properties, are all alike in having a high hygroscopic capacity, while the hydrocelluloses are distinguished by a low moisture content. The two groups differ also as regards solubility in alkalis, and under certain conditions, the hydrated celluloses are resistant to esterifying influences to which normal cellulose responds. Hydrated celluloses are characterised by diminished resistance to hydrolysis by acids to an extent proportional to their degree of hydration. The degree of hydration may be determined in many ways. Schwalbe relies on the copper number and gives the following figures —

	Hygroscopic Moisture	Copper Number after Hydrolysis	Copper Number before Hydrolysis	Difference.
Cotton-wool .	6 1	3 3	1 1	2 2
Cotton-wool mercerised with 8 per cent soda	7 7	3 2	0 9	2 3
Cotton-wool mercerised with 16 per cent soda .	10 7	5 0	1 3	3 7
Cotton-wool mercerised with 24 per cent soda	11 3	6 1	1 2	4 9
Cotton-wool mercerised with 40 per cent soda	12 1	6 6	1 9	4 7

According to Schwalbe's view, the degree of hydration is the same thing as the degree of mercerisation, which is measured also by Knecht's benzo-purpurin and other methods, such as the adsorption of iodine proposed by Hubner, or of alkali from an alcoholic solution of sodium hydroxide (Briggs, *J.S.C I*, 1910, p 622).

Miller (*J.S C.I*, 1911, p. 18) disputed this view, relying chiefly upon the following facts · When the cotton is dried at 95° C. before and after mercerisation, there is no increase in weight but a slight loss. The hygroscopic moisture of mercerised cellulose was found to be the same whether the sample was dried at 95° C in an oven, or at 25° C over calcium chloride Miller held that the existence of a hydrate stable between these two temperatures was hardly conceivable. Further, when dried *in vacuo* over sulphuric acid, mercerised and ordinary celluloses have the same percentage composition. But, having regard to the different properties of mercerised cotton, the author maintains that during mercerisation an isomeride of cellulose is formed, the extent of this conversion depending on the concentration of the alkali used

Cross (*J.S.C I.*, 1911, p 204), criticising Miller's results, pointed out the invalidity of arguments based on the absence of a gain in weight as the result of mercerisation, without taking account of the portion of the cellulose soluble in the alkaline lye, and affirmed that an increase in weight does in fact take place The author, in defending the application of the term "hydration" to this reaction, further argued that the water is taken up by the cellulose in definite quantitative proportions, and that this combination is accompanied by fundamental changes in the physical properties of the cellulose. The hydrates of the celluloses and

their derivatives, which are capable of existing between the temperature of 0° C. and 50° C., are described as definite and well-characterised compounds. If all these yield the same anhydrous cellulose on drying at a high temperature, this fact may be regarded as analogous to the production of the same anhydrous salt by heating the various crystal hydrates, say of sodium sulphate

Miller (*J S C I*, 1911, p. 413), replying to these criticisms by Cross, supports his statement that cotton cellulose shows no gain in weight on mercerisation, by further determinations in which precaution was taken to recover any cellulose lost in the lye The results, calculated on dry weights, were mercerised product, 99·6, fibres, etc, recovered from the lyes after neutralisation, 0·26; loss, 0·14 per cent. of the original cellulose taken The matter recovered from the lye could in no sense be regarded as dissolved cellulose, but consisted mainly of fibres and debris. The moisture of mercerised cellulose, in equilibrium with air at the ordinary temperature, is readily given off in a desiccator over calcium chloride and is not chemically fixed. It is well known that free water and water fixed in solid chemical hydrates evaporate with a constant velocity at a constant temperature under a constant tension of aqueous vapour lower than the saturation-point The author subjected cotton, mercerised in a 30 per cent lye, and containing at the ordinary temperature 1·8 molecule of adsorption water per $C_{12}H_{20}O_{10}$, to the conditions stated above under a bell-jar with calcium chloride. Weighings were made at intervals over forty-eight days, and the results showed that the rate of evaporation of the adsorption water was by no means constant, but diminished rapidly from day to day over the whole period of observation

In all of these experiments bleached cotton was, as a rule, employed Hubner (*J Soc Dyers and Col*, 1925, p. 10) extended his experiment to cotton in the scoured and grey states, and to the effects of caustic soda solutions of high concentration, *i e* from 70° to 100° Tw Both fabrics and yarn were used

The hygroscopic moisture after treatment was determined as follows After immersion in the caustic soda solution, the sample was washed, scoured, and again washed It was then exposed to air for four weeks, after which the amount of moisture present was determined in the usual manner The results showed conclusively that both yarns and fabrics, after treatment with caustic soda of different concentrations, contain more moisture than the untreated material and further, with one exception, viz that of 10° Tw., the amount of moisture increases with the concentration of the caustic soda used The maximum moisture content is reached in the case of yarns at 50° Tw, whilst in the case of fabrics a slight increase takes place between 50° Tw and 60° Tw The moisture values for yarn are greater than those for fabrics, and, further, the most marked increase, particularly in the case of yarns, occurs between 20° Tw. and 30° Tw. When samples were dried at 100° C and then exposed to air, the regain was practically the same for all concentrations of caustic soda used Both scoured and bleached yarn showed a decrease in the copper number at 70° Tw. From 70° to 80° Tw there is an increase, after which up to 100° Tw a further decrease occurs

Recovery of caustic soda plays an important part in the mercerisation process The excess of concentrated liquor is made up to strength and used again The wash liquors are filtered, sometimes recausticised with lime, and concentrated. The following description of a recovery plant for piece goods is given by Chase in the *Dyer and Calico Printer*, 1924, p. 134 (fig 52) —

The main features consist of storage tanks for weak and strong caustic liquors, a series of open gravity filters for purifying the solutions, a vacuum multiple effect evaporator for concentrating the weak filtered washings, a tank for dissolving solid caustic, and the necessary pumps and pipes.

The chief point of departure from other types of recovery systems is the elimination of chemical treatment for the purpose of purifying the wash liquors The common practice is to treat the recovered caustic solutions with lime in either a U-tank or a cylindrical tank with agitating paddles; after more or less heating and stirring the agitation is stopped and the sludge allowed to settle, sometimes at this point a coagulant such as lead acetate is added to hasten the precipitation Finally, the clear liquor is drawn off and the sludge dropped to the sewer or disposed of otherwise.

The filtration system of purification, while giving as good practical results as the chemical method, is not only lower in initial cost and cost of maintenance, but also permits the reclamation of a larger percentage of caustic by the elimination of the loss as sludge

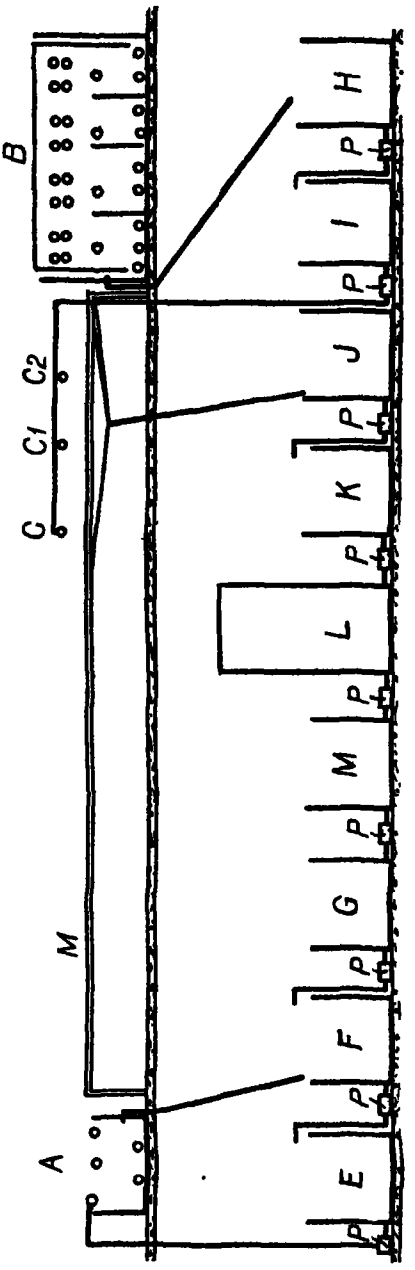


Fig. 52.—Recovery plant

Plan and Layout of System.

To ensure an adequate caustic supply and recovery system for a mercerising department it is necessary to determine the following factors —

1 The quantity of caustic which must be supplied to the mercerising machines

2 The amount of caustic which can be recovered as washings

3 The volume of water which must be evaporated.

Fig 53 illustrates the layout of a caustic supply system designed to meet the requirements of a mercerising department having five ranges with a combined capacity production of 750,000 yards of cloth in fifty hours. By varying the size or number of the several units indicated, this system may be adapted to a plant of any size

Referring to the illustration, A indicates mercerising pad of usual construction; B, recuperator or counter current wash-box; C, spray pipes; D, trough to catch wash liquors; E and I, rectangular mild steel tanks, each 7 by 5½ by 8,

for circulating caustic solutions; G and L, cylindrical mild steel tanks, 7 by 8, for caustic storage, F, open filters of crushed coke, each 7 by 5½ by 8; H and J,

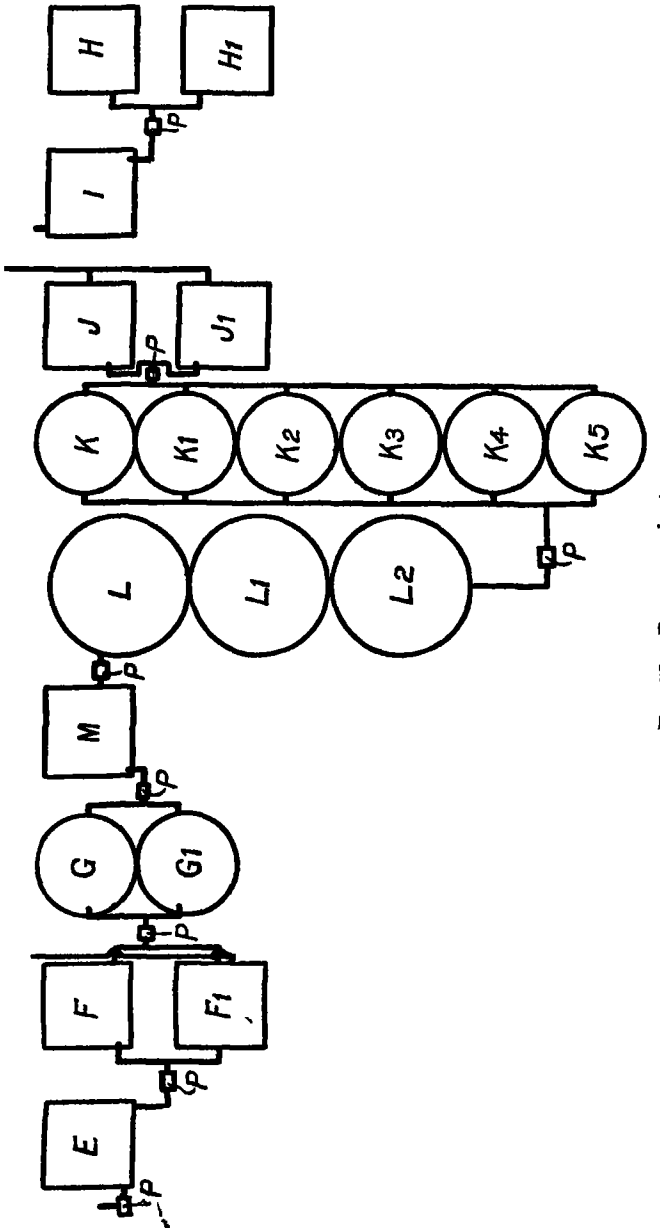


FIG. 53.—Recovery plant.

open filters of crushed quartz, each 7 by 5½ by 8; L, multiple-effect vacuum evaporator; M, tank for dissolving caustic, 7 by 5½ by 8, fitted with steel grate 2 feet from top; and P, pumps.

The units of the system which merit detailed description are the wash-boxes, the open filters, and the evaporator. The wash-boxes or caustic recuperators are of cast iron, having hinged covers at the top and doors at the side to permit ease of access for cleaning or repairs, or for threading of cloth in case of breakdowns. Water is sprayed on the cloth as it leaves the recuperator, proceeds countercurrent to the cloth, removing alkali, and overflows at the front end of the box.

Perforated steam pipes fitted between the guide rollers allow steam to be sprayed on the goods, and squeeze rollers set above the upper guide rollers assist in the removal of the caustic from the cloth. The fact that the recuperator has water seals at each end allows a slight pressure to be maintained

The open filters consist of mild steel tanks fitted with false bottoms of perforated steel placed about 1 foot above the real bottom. Outlet pipes beneath the false bottom for the filtered caustic solution are necessary, together with an outlet line for wash water and at the top an overflow pipe to the sewer. For filtering concentrated caustic solutions the most satisfactory filter bed has been found to be one constructed of crushed coke graded to about the size of a pea.

The filter bed for dilute alkali liquors is preferably made of crushed quartz about the size of rice kernels. Care must be taken that the perforations in the false bottoms are sufficiently small to prevent the passage of the materials used in building the filter bed. It is advisable to instal the filters in duplicate, since this admits of constant filtering, one filter of a pair being in use while the other is being washed

For a plant of the size described the vacuum evaporator should be of the multiple-effect type, having either three or four effects In a plant of smaller size an evaporator with one or two effects will prove more economical. The evaporator may be of either the vertical or the horizontal tube type; the chief consideration is that it be of sufficient capacity to concentrate the total volume of recovered weak caustic solution to the required strength Heat loss by radiation will be largely prevented if the evaporator is properly insulated.

Caustic Flow.—By referring to fig 53, the flow of caustic through the processes of mercerisation and reclamation can be followed Tank E contains caustic soda at a strength of not less than 52° Tw., which is pumped to the mercerising pads Circulation of the caustic is maintained in the pads for the purpose of keeping the alkali at a constant strength. The excess liquor flows by gravity to coke filter F or F1, and after filtering is pumped into tank E. Simultaneously with the filtering of this overflow liquor, caustic at 76° Tw. is drawn through the filter from storage tank G or G1, to maintain the concentration and volume of the liquor in tank E

The overflow from the recuperator B passes through quartz filter H or H1 into tank I, from this tank it is pumped through spray pipe C to the cloth passing over the tenter The liquor percolates through the cloth, removing caustic, is caught in trough D, and then flows by gravity through quartz filter J or J1 After filtering, these caustic washings are pumped into storage tanks K to K5, and from these to the evaporator L The hot concentrated liquor from the evaporator is pumped into dissolving tank M, where solid caustic is added to bring the concentration to 76° Tw., and to replace the loss of alkali from the system. Finally, the concentrated liquor is pumped into tank G or G1, thus completing the cycle.

To mercerise 150,000 yards of cloth will require the feeding in of approximately 2000 gallons of alkali solution at 76° Tw., containing the equivalent of 8000 lbs. of solid caustic. The proper washing of the cloth in the recuperator requires the introduction of about 15,000 gallons of water. After circulating

through the cloth on the tenter this wash liquor should be at approximately 10° Tw Some 13,000 gallons of water are evaporated, leaving 2000 gallons of concentrated solution at 69° Tw , containing the equivalent of 6000 lbs. of solid caustic. The addition of 2000 lbs. of drum caustic in the dissolving tank suffice to bring the concentration to 76° Tw. and replace the loss from the system

Limit of Recovery.—A reclamation of 75 per cent of the total caustic used is readily obtainable under these conditions By supplying a larger amount of wash water still further recovery is possible, but the increased cost of evaporation makes this undesirable For example, by using 30,000 gallons of wash water about 90 per cent recovery can be obtained, the wash liquors in this case being reduced to a strength of 5° Tw In order to concentrate these washings to 69° Tw., both the size of the evaporator and the steam consumption must be doubled, with the result that the cost of reclaiming the additional 15 per cent. or 1200 lbs. of caustic averages 4 cents per lb , or more than the price of new caustic

It may be stated, therefore, that while 90 per cent recovery is possible, from the standpoint of economy a reclamation of 75 per cent of the caustic used is the most practical Again, when goods are mercerised in the grey, the alkali remaining in the cloth as it leaves the wash-box is utilised in the subsequent kier boiling, and this caustic may be properly charged to the latter process



Fig 54.—Mercerised cotton

Operation of Supply System.—Two men are required to operate a system of the type described One man is in charge of the evaporator The other is responsible for the washing and care of the filters, and is also responsible for the maintenance of the various caustic solutions at the strength designated. It is desirable that each of these men be trained in the duties of the other, so that in the case of the absence of one the system may continue to function properly.

The Microscopic Structure of Mercerised Cotton.—The process of mercerisation is accompanied by an important change in the microscopic structure of the fibre These have been studied fully by Pope and Hubner (*J S.C I* , 1904, p 408), from whose paper the following details are taken If some cotton fibres are treated under the microscope with cold concentrated sodium-hydroxide solution, they will be seen to swell and then gradually untwist, till they appear like swollen tubes instead of twisted cells If this experiment be carried out under tension, caused by fixing the ends of the fibre to the slide with wax, the untwisting of one portion of the fibre causes the twisting of another part, thus forming straight tubular fibres with a series of ridges on their surface. These ridges are the cause of the increased lustre of mercerised cotton according to Pope and Hubner The microscopic appearance of mercerised cotton is seen in fig. 54

Other observers, including Harrison (*J S.C.I.*, 1915, p. 1087), maintain that the increased lustre of mercerised cotton is caused, simply, by the smooth, straight surface of the tubular fibre, which has a high reflecting power. Harrison finds no evidence for the ridges described by Pope and Hübner. Knecht, Rawson, and Loewenthal (*Manual of Dyeing*, vol. i. p. 37) state that when cotton yarn is

mercerised under tension, and is still saturated with sodium hydroxide, it acquires a gelatinous and to some extent a plastic condition, so that the hairs become rounded and more translucent, are drawn out and stretched, and are set, in this state, by subsequent washing. Consequently, in the finished yarn a large proportion of stretched and straightened hairs, of a more or less round section, lie parallel to each other, so that reflection tends to become specular and the inherent lustre of the hairs becomes apparent to the eye

Adderley (*J Text. Inst*, 1924, T 195) states that it is a well-known fact that certain varieties of cotton have a marked lustre ascribed often to their fineness. But photometric measurements show that the only physical factor which affects lustre is the shape of the cross-section. Cotton hairs which tend to be circular in section are more lustrous than flattened hairs This accounts for the superior lustre obtained on mercerising, especially under tension. This is illustrated in fig 55

Willows and Alexander (*J Text Inst*, 1922, T 237) investigated the changes

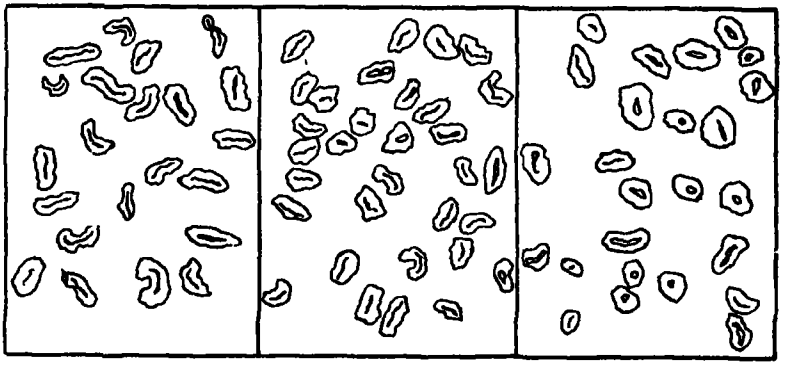


FIG 55 —Cross-section of mercerised cotton

in area and volume of thin sections of cotton hairs when mercerised This was done by projecting the image of the section on to a screen at a magnification of about 700 diameters The area of the section was deduced from the weight of paper, weighed under constant conditions, covered by the image In this way areas were measured of sections (1) dry, (2) wetted with water, (3) mercerised, (4) washed with water, (5) dried, (6) wetted a second time with water. The increase of area on the first wetting was found to be from 40 to 42 per cent. The graphs show that the curve for the mercerised sections has two peaks for both change in area and volume, viz one for 25° Tw lye and the other for lye of 45° Tw, the percentage increase in area being approximately 210 per cent. and 290 per cent. respectively, and the percentage increase in volume 190 per cent and 270 per cent It was found that the inner part of the hair bulges out over the cuticle at the ends of the section. This bulging begins with solutions of 25° Tw and is very pronounced with lye of 30° to 40° Tw. It is due to swelling of the cellulose before the cuticle is sufficiently softened to permit the full volume to be reached. If the cuticle has been damaged no bulging occurs, hence, this may be made use of for the detection of tendering

Tests for Mercerised Cotton.—*It is often important to be able to determine*

whether cotton has been mercerised, and, if so, its degree of mercerisation. The following tests may be used —

1 A portion of the sample is mounted on a microscope slide and examined under the microscope for tubular fibres The degree of mercerisation may be estimated by counting the proportion of twisted and tubular fibres

Herzog (*J S C.I* , 1915, p. 487) has applied a similar test to determine the capacity of cotton yarns for mercerising. Lack of lustre on mercerisation may generally be traced to the presence of incompletely ripened or otherwise abnormal fibres In order to test the mercerising capacity, sections of the raw yarn about 0·5 mm long (*i e* ten separate sections) are mounted in a mixture of potassium hydroxide and glycerin on slides ruled with fine lines to facilitate counting In each mount one hundred fragments are counted, without selection, those which fail to show a perfectly cylindrical form being reckoned as non-mercerised The proportion of cylindrical fragments is in direct relation to the lustre obtainable, *e g* very high lustre, 93 to 98 per cent , satisfactory, 83 to 87 per cent ; inferior, 68 to 75 per cent.

2 *Knecht's Test* —A sample is boiled in a 0·5 per cent. solution of benzo-purpurin for thirty minutes side by side with a similar sample of unmercerised cotton It is then washed well in water and the colours compared. The mercerised cotton will be dyed more deeply than the unmercerised sample

3 *Knecht and Knagg's Test* —Ordinary cotton dyed with benzo-purpurin turns blue when treated with hydrochloric acid; mercerised cotton, unless excess of acid is used, remains red or reddish violet The test may be carried out by dyeing the sample, together with a piece of ordinary cotton, with benzo-purpurin, and then adding hydrochloric acid, drop by drop, till the unmercerised cotton just turns blue The mercerised cotton will remain a bright red colour

4. *Lange's Test* — Prepare the following solutions (*a*) 5 grammes of potassium iodide and 1 of iodine dissolved in 16 c c water, (*b*) 25 grammes of zinc chloride in 12 c c water Mix these solutions and allow the mixture to stand to settle. Then decant off the clear liquid for use. A portion of the sample to be tested is soaked in the reagent for about three minutes. Both mercerised and unmercerised cotton will become brown Remove the sample and wash it with boiled and cooled distilled water until the brown colour, due to excess of iodine, has changed to dark blue-black Now place the sample in fresh water Unmercerised cotton will lose its colour very quickly, while the bluish colour persists for a considerable time in mercerised cotton Schreinerised cotton, in which lustre is produced by purely mechanical means, gives negative results with these tests

5 *Hubner* (*J S.C I* , 1908, p 105) has proposed a method founded upon the zinc chlor-iodide reaction, of measuring quantitatively the degree of mercerisation, *i e* the strength of the alkali used

The following solutions are required —

(*a*) 1 gramme iodine and 20 of potassium iodide in 100 c c water
(*b*) 280 grammes zinc chloride in 300 c.c water.

Just before use, three mixtures of these are made containing 5, 10, and 20 drops of the iodine solution in 100 c c. of the zinc-chloride solution. Portions of the sample are then immersed in these mixtures, and the colour produced is noted and compared with those given in the following table —

Strength of Sodium Hydrate used to Mercerise	5 Drops to 100 c c	10 Drops to 100 c c	20 Drops to 100 c c
0°	Colourless.	White	Slightly red
10°	Faintly blue	Faint brown.	Faint reddish chocolate
20°	,,	Chocolate brown	Bluish chocolate
30°	,,	Reddish blue.	Dark reddish navy blue.
40°	Very light blue	Darker than 30°.	Black
50°	Much stronger blue		
60°	Same as 50°.		
70°	Lighter than 60°		

6 *Knecht* (*J Soc. Dyers and Col*, 1908, p 67) measures the degree of mercerisation by dyeing the sample with benzo-purpurin and estimating the percentage of dyestuff absorbed by titration with titanous chloride solution Full details of the method of titration will be found in Knecht, Rawson, and Loewenthal, *Manual of Dyeing*.

The following table is given —

Strength of Sodium Hydroxide used for Mercerising	Percentage of Benzo-purpurin in Fibre
10° Tw	1 88
20° ,,	2 39
30° ,,	2 57
40° ,,	3 15
45° ,,	3 27
50° ,,	3 38
55° ,,	3 50
60° ,,	3 56
65° ,,	3 60
70° ,,	3 66
Unmercerised cotton	1 77

The Schreiner process and other mechanical fin calendering and beetling, produce also a lustre on pu by the Schreiner process may be mistaken for the e the fabric does not give the chemical tests for merc same microscopic appearance. In schreinerising th ence of moisture till it assumes a plastic conditi pressed by means of a heated calender engraved wi of which runs obliquely to the length of the clot engraved or embossed with fine diagonal lines wh be invisible to the naked eye. Their effect is lustre, owing to their power of reflecting light fro

The Action of Salts.—Cellulose adsorbs c This is illustrated by copper sulphate. Solu concentrations and temperature, are first ads

to swell up and assume a colloidal condition. In many cases solution is effected Thus thiocyanates (particularly calcium thiocyanate), zinc chloride, and potassium mercuric iodide all produce rapid swelling, gelatinisation, and finally solution

Von Weimarn (*J S C I*, 1912, p 768) found that different kinds of cellulose can be converted into a gelatinous plastic condition or into a (dispersoid) colloidal solution by treatment with solution of salts under suitable conditions In a later paper (*J Soc. Dyers and Col*, 1923, p 306) he states that any salt solution is capable of producing this effect at a suitable temperature and pressure. With certain salts, such as the iodides and thiocyanates of the alkali metals or alkaline earths, this change is produced at ordinary temperatures and pressures With a concentrated solution of sodium chloride, peptisation of the cellulose begins at about 170° C and 8 atmospheres pressure Solutions of cellulose containing only about 1 per cent of cellulose set to transparent or semi-transparent jellies on cooling, and, if the jellies are left exposed to the air, the salts effloresce and a skeleton jelly of hydrated cellulose is left The experiments of Pope and Hubner may be referred to also They found that a cold saturated solution of potassium iodide rendered cotton hairs glassy and transparent, producing swelling and shrinking without untwisting, while a saturated solution of potassium mercuric iodide caused rapid swelling, gelatinisation, and ultimately solution A 40 per cent solution of zinc chloride at a moderate temperature acts in the same way, *first gelatinising and then dissolving cellulose, forming a thick viscous solution* Von Weimarn's conclusions have not, however, been universally accepted Herzog and Beck (*J S C I.*, 1921, 254A) are of opinion that the solubility of cellulose in concentrated salt solutions is a function of the hydration of the ions of the respective salt The ions may be arranged in the order –

(1) $NH_4 < K < Na < Li$.
(2) $Ba < Sr < Ca$
(3) $\frac{1}{2}SO_4 < Cl < Br < I < CNS$

h raw and purified cotton no swelling or solution occurred
es, bromides, nitrates, sulphates, thiocyanates, acetates,
n, potassium, ammonium and magnesium, barium and
d barium thiocyanate Calcium nitrate attacked the
out disappearance of structure was observed in solutions
20 to 150° C Solution of the cellulose took place in
e, lithium chloride, bromide, iodide and nitrate, calcium
anate, strontium thiocyanate, and potassium mercuric
re " calcium chloride dissolves cellulose if the solution
100 hydrochloric acid and then concentrated
and Col, 1912, p 359) has shown that when sodium-
through cotton, hydrochloric acid passes through
and Col, 1923, p 22) washed cotton with fresh dis-
gave the same neutral reaction with methyl orange
was then treated with a neutral solution of sodium
ate was acid in all cases, and the acidity decreased
salt solution. But if, after treatment with salt
neutral, the cotton was washed with water, till
acid filtrates were obtained again on treatment
be repeated several times The aqueous wash-
ution, were alkaline, the alkalinity decreasing
nd being very difficult to remove completely.

The total alkali obtained was nearly equivalent to the acid extracted by the salt solution. Preliminary treatment, such as extraction with alcohol or ether, washing with acid or alkali, did not affect the results. Barium and calcium chlorides acted in a similar manner, but less acid was produced.

The most important solvent for cellulose is Schweitzer solution, a solution of copper oxide in aqueous ammonia, which contains the compound $Cu(NH_3)_4(OH)_2$. But it does not dissolve cellulose without change. Traube (*J Soc Dyers and Col*, 1924, p. 17) used cupric ethylenediamine, since ammoniacal cupric oxide cannot be freed from ammonia He found that alcoholates were formed with polyhydroxy compounds, such as copper ethylenediamine glycerate, which has the formula

$$\left.\begin{matrix} HO.CH_2\ CH(OH)CH_2O \\ HO\ CH_2.CH(OH)CH_2O \end{matrix}\right\rangle [Cu(en)_2]$$

This body reacts with more copper, giving cupric compounds. Thus:

$$[Cu(en)_2]\left\langle \begin{matrix} OH_2C\ CH(OH)\ CH_2OH \\ OH_2C.CH(OH)CH_2OH \end{matrix}\right. + [Cu(en)_2](OH)_2$$

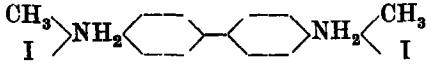
$$= [Cu(en)_2]\left\langle \begin{matrix} OH_2C\ CH(OH).CH_2O \\ OH_2C\ CH(OH)\ CH_2O \end{matrix}\right\rangle Cu + 2H_2O + 2en.$$

He showed that free ethylene is formed The action of cuprammonium solution on cellulose is analogous, forming, first, copper-ammonia cellulose alcoholate and then the cupric compounds, while the liberated ammonia can dissolve more cupric oxide and cellulose, the process going on till a highly viscous solution is obtained.

The Action of Dyestuffs.—Cotton has no affinity for the acid and basic dyestuffs, unless previously mordanted with a basic or acid mordant respectively. Over-bleached cotton is dyed, however, by basic dyestuffs from a cold bath, the depth of colour obtained depending upon the degree of over-bleaching Mercerised cotton has also a certain amount of affinity for basic dyestuffs Direct and sulphur dyestuffs dye cotton from either a cold or boiling bath, the affinity of mercerised cotton being still greater The dyeing of cotton by these colours is probably a physical phenomenon. Witt (*J.S.C.I.*, 1891, p 42) and Cross and Bevan (*J S.C I*, 1894, p 354) held that the dyeing is due to the formation of a solid solution of the dyestuff in the fibre. The dyestuff is, according to this view, more soluble in the fibre than in water, and is consequently extracted from its aqueous solution, the function of the salt used being to render the dyestuff less soluble in water and consequently relatively more soluble in cellulose Congo red gives a yellow aqueous solution but dyes cotton red. Witt held that this is analogous to the extraction of iodine from water by means of chloroform with the change from a brown to a violet solution. Weber (*J.S C.I.*, 1894, p 120) stated that direct dyestuffs attach themselves to cotton as molecules, while Gnehm and Rotheli (*J.S C.I*, 1898, p. 660) confirmed this view by dyeing cotton with the barium salt of certain direct colours, the amount of barium in the dyed cotton corresponding to the quantity of adsorbed dyestuff. Gnehm and Kaufler (*J.S C I.*, 1902, p. 611) showed that the free acids of the direct dyestuffs would also dye cotton. The fibre was dyed with both the free acid and sodium salt of benzo-purpurin. That dyed with the salt was then washed with hydrochloric

acid, when it became blue. When all the sodium salt had been washed out, however, the original colour was permanently restored. Bilz (*J.S.C.I.*, 1904, p. 439) showed that colloidal solutions of selenium and gold acted in the same way as those of direct dyestuffs towards cotton, and concluded that the explanation was to be found in the formation of adsorption compounds. Both increasing the temperature and addition of salt to the bath caused colloidal solutions of these elements to dye the cotton more deeply. The presence of a protective colloid, on the other hand, caused dyeing to become slower. Hubner (*J.S.C.I.*, 1907, p. 866) made experiments with various inorganic substances, such as charcoal. Charcoal and graphite were treated with benzo-purpurin 4B and then topped with night blue The results of these experiments led him to the conclusion that dyeing with direct dyestuffs is a purely mechanical process. But the physical or mechanical theory is not the only one When the hydroxyl groups of cellulose are replaced by acetyl groups its affinity for direct dyestuffs is destroyed, returning again if the hydroxyl groups are replaced. It appears, therefore, as if the direct dyestuffs had some affinity for these hydroxyl groups. Vignon (*J.S.C I*, 1897, p 1014) maintained that the action was a chemical one, depending on the presence of the groupings >N—R—N< or >N—N<. During dyeing the nitrogen atoms become pentavalent, giving the system $>\hat{N}.R.\hat{N}<$ or >N—N<.

Tetramethyl benzidine is taken up by cotton, but the fibre has no affinity for the methiodide of this body, which contains pentavalent nitrogen, as shown by the formula



Binz and Schroeter (*J.S C I.*, 1903, p 1126) think that dyeing with direct dyestuffs may be considered as a condensation of the quinonoid nucleus of the dyestuff with the fibre.

Artificial Silk.—All kinds of artificial silk are derived from cellulose. It is characterised by a lustre approaching that of true silk It is suitable for the manufacture of all kinds of fabrics either alone or mixed with other textile fibres. It can be produced in threads or filaments of great fineness, and has considerable tensile strength and elasticity The importance of the artificial silk industry may be judged from the fact that, according to the *Chemical Age*, 1922, p 522, fifty tons per day are being manufactured in Europe and America.

There are four distinct varieties, viz.—

1. Nitrocellulose or Chardonnet silk.
2. Cuprammonium silk or lustracellulose
3. Viscose silk.
4. Cellulose acetate or acetyl silk.

The first process for the manufacture of artificial silk consisted in dissolving cellulose in a solution of zinc chloride and precipitating it in a bath of water. This process has, however, never obtained any commercial importance.

Nitrocellulose silk was discovered by Chardonnet in 1884 It was made
iginally from gun cotton. When cellulose or cotton is treated with a mixture
tric and sulphuric acids, esters or nitrates of cellulose are obtained There
ar
veral of these, but under suitable conditions a mixture consisting
of n
of the tetra- and penta-nitrates is obtained. $C_{12}H_{16}(NO_3)_4O_6$;
are s
$O_3)_5O_5$. The sulphuric acid acts as a condensing agent, as in the
chiefly
$C_{12}H_{15}(N$

formation of esters from simple alcohols. Thus ethyl acetate is obtained when alcohol is heated with acetic acid and sulphuric acid—

$$C_2H_5OH+CH_3COOH=C_2H_5OOCCH_3+H_2O.$$

Although the nitrates of cellulose are insoluble in water, they dissolve readily in mixtures of alcohol and ether, giving viscous solutions when sufficiently concentrated. The purity of the original cellulose is of importance. Hydrated or mercerised cellulose gives more viscous solutions than ordinary cellulose. The proportions of acid used and the temperature of the reaction determine largely which nitrocellulose is produced. After nitration, the excess of acid is washed away with water. The washed residue is then pressed or centrifuged till it contains about 33 per cent. of water and dissolves in the solvent. The solution is filtered under pressure and allowed to stand to "ripen" or become more viscous. This ether-alcohol solution is then forced through fine jets, at a pressure of from 2 to 3 atmospheres, either into a chamber of warm air or a bath of water. In the first case the solvent evaporates, leaving a thread of coagulated cellulose. The air, charged with the solvent, is led through condensers, where the solvent is recovered. When a bath is employed, the solvent is washed away and the thread precipitated. But it is difficult to recover the solvent from water. When a mixture of cresols is substituted, the solvent can be distilled off at 150° C.

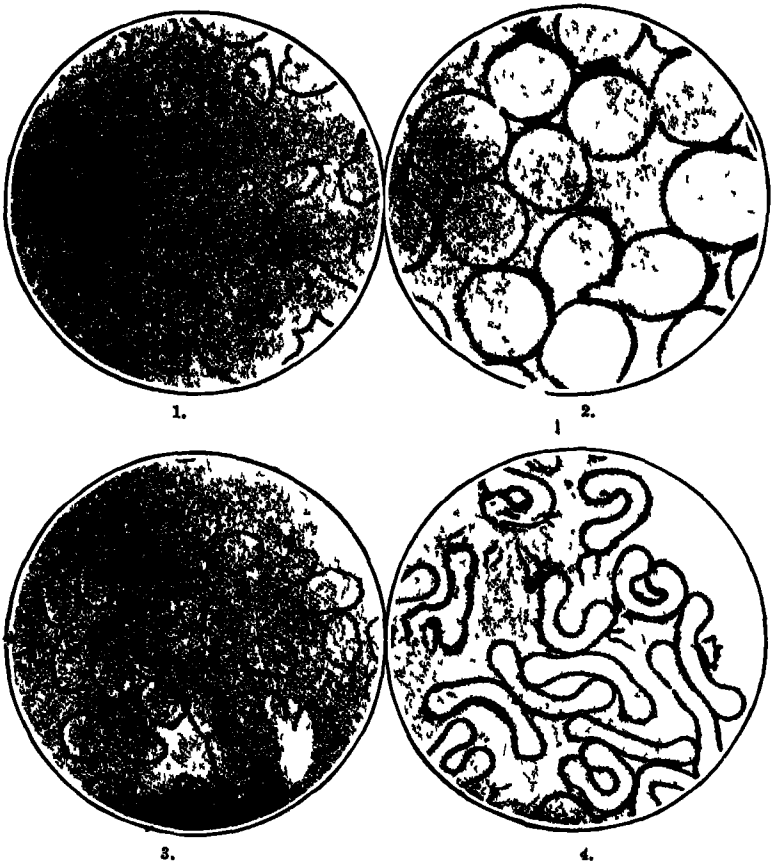
According to Chardonnet (*J.S.C.I*, 1918, 650A), the cross-section contours of artificial silks are a characteristic indication of the physical conditions of spinning, and therefore a useful guide in the identification of their origin. The first basis of classification is the manner of coagulation, viz. by evaporation of the solvent and by precipitating liquids. Other things being equal, threads formed by precipitation tend to be neither so strong nor transparent as those formed by evaporation, since precipitation implies discontinuity As a rule, silks formed by precipitation show a more or less circular contour in their cross-sections. Those produced by drying are irregular, and exhibit peculiarities which influence their industrial use. Collodion silks are made by the Chardonnet process in both ways. When spinning by coagulation in water, a very fluid collodion is employed, containing about 50 grammes per litre. The cross-sections of threads spun in this manner show re-entrant angles (fig. 56), and have generally a stellate contour This is because when the fluid threa emerges in a cylindrical form from the spinning orifice it is immediately coagulat on contact with water, and the film, thus formed, although very thin, preserig) its integrity and, during its drying, is folded up on itself as the cross-sectined area becomes reduced to correspond with the final volume of the solid threarmula

The irregularities of the cross-section are not so noticeable when a collodion is spun by this method, since the ratio of the original to the finalder the is less. asionally,

When spinning into air, much more viscous solutions, up to 250 detected. per litre, are employed. Coagulation takes place much less rapidised by the final solid thread has a larger sectional area. Hence it follows that 7. Herzog is much less wrinkled and cross-sections have a flattened, curved silks, with the

The covering power of silk increases in inverse ratio to its ap s, the spectro- and, other things being equal, silks with round and regular conl. space than those with irregular contours. In this respect collacial silk When cularly those spun in water, possess an advantage; but otkure of 1 part of have favoured the process of spinning in air After spinningic acid for twenty- thoroughly to remove any residual acid or solvent. Butnsisting of cellulose

and solvent are highly inflammable. To reduce the inflammability, the silk is next denitrated by treating it with a solution of ammonium sulphide and again washing This removes the NO_2 groups, replacing them by hydroxyl (OH). Thus the final product consists of re-precipitated cellulose. The term nitrocellulose is inaccurate. In a nitro compound the nitro group is connected directly to a carbon atom, as in nitrobenzene, $C_6H_5NO_2$. When a nitro compound is



1 Chardonnet silk. 2. Cuprammonium silk 3 Viscose silk. 4 Cellulose acetate silk.

FIG 56 – Cross sections of artificial silk

th a reducing agent an amine is produced. Thus nitrobenzene when es aniline, $C_6H_5NH_2$ In nitrocellulose the nitro group is attached n atom, as it is in ethyl nitrate, $C_2H_5ONO_2$. When such compounds lcohols are obtained.

n in the case of trinitrocellulose is

$$(ONO_2)_3+12H_2S=C_{12}H_{17}O_7(OH)_3+3NH_3+6H_2O+12S.$$

es not remove the whole of the nitro groups. Sufficient remain coloration with diphenylamine and sulphuric acid. This identify Chardonnet silk. Denitration also reduces both

the weight and lustre of the silk. Chardonnet, Lehner, and Du Vivier silk are all made from nitrocellulose. They are characterised by great lustre and a marked affinity for basic dyestuffs. The latter property is due to the presence of small quantities of residual nitro or sulphuric acid groups. Like other kinds of artificial silk, nitro silk loses much of its tensile strength when wet but recovers it again on drying. Pentecost has recorded that nitro silk is liable to become tender on storing. Heermann (*J.S.C.I.*, 1913, p 80) observed the same effect, which is indicated by milky-white specks containing sulphuric acid. He attributes these to the formation of unstable sulphuric esters of cellulose. But the presence of these esters can only cause tendering if they are of an unstable type. Heermann describes the following test as suitable to determine the stability The silk is washed with distilled water till perfectly neutral. It is then heated for an hour in a drying oven at 135° to 140° C. and examined for free sulphuric acid or brown or black stains. The presence of either of these denote unstable esters which may cause damage on storing.

Briggs (*J S C I*, 1913, p. 282) states that the esters containing little sulphuric acid can be washed with water till the washings are neutral, whilst the ester has the properties of an insoluble acid. As the percentage of combined sulphuric acid increases the esters become less stable towards water, and the higher members of the series assume a colloidal form and continually split off free acid If nitrocellulose, containing a small amount of combined sulphuric acid, be boiled for a long time with water or acid water, the sulphuric ester is gradually hydrolysed and the cotton becomes stable But if washed with alkaline water the acid sulphuric ester combines with the base, giving neutral salts which are comparatively stable towards boiling water. Such nitrocelluloses are dangerous, because on treatment with acid at any subsequent stage (*i.e.* bleaching or dyeing) the base is removed and the unstable free acid ester reproduced. The combined sulphuric acid is in the form of an acid cellulose ester of the general formula $HSO_4(X)_n$, where X represents the cellulose nitrate or acetate.

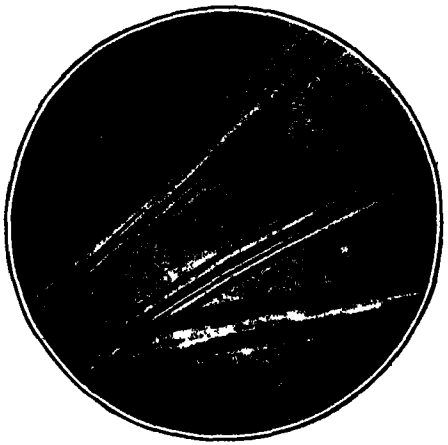


FIG 57.—Viscose silk

Microscopic Structure of Artificial Silk.—When examined under the microscope nitro silk is seen to consist of a structureless fibre. Occasionally, when prepared by the evaporation method, minute air-bubbles may be detected. The surface exhibits generally longitudinal marks or striations, caused by the ridges and indentations referred to above. These are seen in fig. 57. Herzog and Gonell (*J. Text. Inst.*, 1925, 85A) state that all artificial silks, with the exception of cellulose acetate, show, when examined with X-rays, the spectrographic diagram of a crystalline structure symmetrically disposed

Nitrocellulose is used for other purposes besides making artificial silk. When cellulose or purified cotton is soaked in 10 parts of a cold mixture of 1 part of nitric acid (sp. gr. 1·5) and 3 parts of concentrated sulphuric acid for twenty-four hours and washed thoroughly with water, the residue consisting of cellulose

hexanitrate, $C_{12}H_{14}(NO_3)_6O_4$, is known as gun cotton. Gun cotton mixed with nitroglycerin is the basis of cordite. Collodion is a solution of cellulose nitrated in alcohol and ether. Cellulose nitrates when heated under pressure with camphor form celluloid When cellulose nitrates are heated with a solution of potassium hydroxide, they are saponified like other esters, cellulose and potassium nitrate being produced—

$$C_{12}H_{17}O_7(NO_3)_3+3KOH=C_{12}H_{17}O_7(OH)_3+3KNO_3.$$

Cuprammonium silk (lustracellulose, Glanzstoff or Pauly silk) is made from a solution of cellulose in Schweitzer's solution. Cotton is boiled, under pressure, with a dilute solution of sodium hydroxide and sodium carbonate, washed and bleached with sodium hypochlorite. It is then washed, treated with an antichlor, such as sodium thiosulphate, again washed and centrifuged till it contains about 50 per cent of water. The residue is dissolved in cuprammonium solution This is made by covering copper turnings with a 14 per cent solution of ammonia and passing air through at a low temperature (4° C) A little copper sulphate and sodium hydroxide may be added to raise the copper content. The solution of the cellulose takes some days, a strength of about 45 grammes per litre being necessary This is filtered under pressure, and, after "ripening," forced through nozzles into a spinning bath which may consist of either (*a*) acid or (*b*) sodium hydroxide and glucose. When an acid bath is used the ammonia is neutralised and the copper oxide dissolves in the bath as a salt of the acid used. After a time the bath becomes deeply coloured by the copper, making the thread difficult to see If a bath of sodium hydroxide and glucose be employed, the copper is precipitated as insoluble cuprous oxide, which collects at the bottom of the vessel After spinning, the thread is treated with acid to remove the last traces of copper and then washed Cuprammonium silk consists of smooth, rounded filaments with a hard glass-like lustre Its cross-section is as a rule oval or round Its microscopic appearance is much the same as that of nitro silk

Viscose silk is made from wood pulp and not from cotton. Hence it starts from a cheaper raw material Moreover, it has a greater covering power, lustre, and resistance to finishing and dyeing operations than either nitro-silk or lustra-cellulose. Spruce wood is made into a pulp, boiled under pressure with calcium bisulphite, and then bleached The washed bleached pulp is pressed into sheets, which are used in the manufacture of paper and as a filtering medium. These sheets are the starting-point in the manufacture of viscose. They are soaked in a cold solution of sodium hydroxide, of mercerising strength, and containing sufficient alkali to convert the cellulose into alkali cellulose, $(C_6H_{10}O_5)_2$ 2NaOH. The excess of alkali is pressed out and the residue ground to crumbs. These are kept for some time exposed to air to mature. This is an important part of the process. The addition of a little sodium peroxide to the alkali, or the presence of an oxygen carrier, such as a finely divided metallic, iron, or nickel oxide, accelerates this oxidation. The matured alkali cellulose is then treated with carbon bisulphide in a closed vessel provided with paddles or stirrers. The temperature must be low and air excluded, since carbon bisulphide is both volatile and inflammable

The carbon bisulphide enters gradually into combination with the alkali cellulose, the latter swelling up into a brownish sticky mass of cellulose xanthate This reaction is similar to that which takes place between carbon bisulphide and sodium oxide—

$$CS_2+Na_2O=SC\begin{matrix}ONa\\SNa,\end{matrix}$$

or between sodium alcoholate and carbon bisulphide—

$$CS_2+C_2H_5ONa=SC\begin{matrix}OC_2H_5\\SNa.\end{matrix}$$

The reaction between alkali cellulose and carbon bisulphide may be

$$C_6H_9O_4(ONa)+CS_2=SC\begin{matrix}OC_6H_9O_4\\SNa.\end{matrix}$$

But Wilson (*J.S.C.I.*, 1917, p. 817) gives the formula of the xanthate as

$$SC\begin{matrix}(C_6H_{10}O_5)_n\\NaS.\end{matrix}$$

This cellulose xanthate (or viscose) is dissolved in a dilute solution of sodium hydroxide. The solution thus obtained is kept for some time to "ripen" or become more viscous. This process is due to progressive hydrolysis accompanied by a gradual increase in the value of n or a decrease in the number of xanthate groups. Thus:

$$SC\begin{matrix}(C_6H_{10}O_5)_n\\NaS\end{matrix}\quad\text{first becomes}\quad SC\begin{matrix}(C_6H_{10}O_5)_{n+1}\\NaS.\end{matrix}$$

The process may continue till cellulose is reproduced. The degree of ripeness necessary depends upon such factors as the kind of silk required and the composition of the spinning bath. The ripening is accompanied also by decreasing solubility in water. When sufficient ripeness is obtained the solution is forced through jets into a spinning bath. This may consist of a solution of an acid with or without the addition of salts, such as sodium bisulphite The xanthate is decomposed and a thread of cellulose hydrate is formed. This is washed and bleached. The cross-section of viscose silk is generally irregular in contour, though this depends to a considerable extent upon the method of spinning Its microscopic appearance is similar to that of other varieties (fig 57).

Cellulose-acetate Silk.—When cellulose is heated under pressure with acetic anhydride, acetates of cellulose are produced. The composition of the compounds depends upon the proportion of acetic anhydride used, the temperature of the reaction, and the presence or absence of condensing agents such as zinc chloride. From one to six acetyl groups may be introduced. The tri- and tetra-acetates are the most important. Their formation is represented by the equations

$$C_{12}H_{20}O_{10}+3C_2H_4O_2=C_{12}H_{17}O_7(C_2H_3O_2)_3+3H_2O,$$
$$C_{12}H_{20}O_{10}+4C_2H_4O_2=C_{12}H_{16}O_6(C_2H_3O_2)_4+4H_2O.$$

Cellulose acetates are insoluble in water, but dissolve in glacial acetic acid and certain organic solvents such as acetone, chloroform, and mixtures of chloroform and alcohol. The silk is spun, like nitro silk, by dissolving the acetate in a suitable organic solvent and forcing the viscous solution through fine nozzles into

a warm chamber. Hence its cross-section has a fairly regular contour. Its appearance is shown in fig. 58.

Cellulose acetate is used for other purposes than making silk Owing to its insolubility in water, it is employed for waterproofing textile fabrics and the wings of aeroplanes. It is also used as an insulating medium, since it is a non-conductor of electricity, while on account of its low inflammability it forms a safe material for the manufacture of films. When heated with a solution of an alkali it is saponified with the reproduction of cellulose Thus, with sodium hydroxide—

$$C_{12}H_{17}O_7(C_2H_3O_2)_3+3NaOH=C_{12}H_{17}O_7(OH)_3+3C_2H_3O_2Na$$

This reaction is of importance in the dyeing of acetyl silk. It has no affinity for the direct dyestuffs, but, if it be partially saponified, a sheath of regenerated cellulose is produced which takes up the colouring matter readily. Cellulose-acetate silk has a high lustre and good covering power. Its elasticity and tensile strength are high, and its imperviousness to water is a useful quality. At first the difficulty of dyeing it militated against its use, but this is now being overcome rapidly.

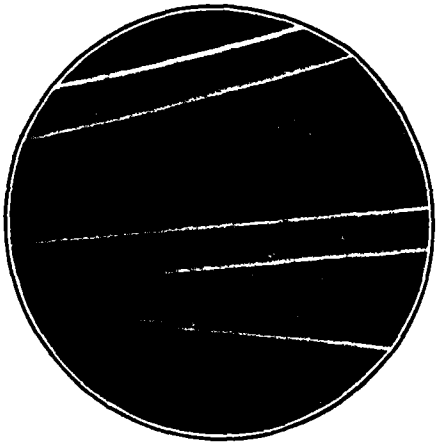


Fig 58.—Cellulose-acetate silk.

It has been noted that all kinds of artificial silks show a great decrease in tensile strength when wet. The following figures, given by Stokes (*J Soc Dyers and Col*, 1922, p. 51), illustrate this The tenacity of artificial silk is generally expressed in terms of the weight in grammes required to break a thread of definite size (generally grammes per dènier), whilst the extensibility is the percentage elongation at the breaking-point

	Tenacity Grammes per Dènier		Extensibility
	Dry	Wet	
Nitro silk . . .	0 75–1 40	0 25–0 60	7 5–16 0
Cuprammonium silk .	1 0 –1 35	0 35–0 55	14–18
Acetate silk . .	1 1	0 7	18
Viscose „	1 2 –1 7	0 45–0 79	11–22
Natural „ .	2 5	2 0	21

Another table, taken from *J. Soc Dyers and Col*, 1923, p 185, shows the count, mean diameter of the fibre (from which is calculated the area of the cross-section), tensile strength when dry and when wet, and elasticity in both wet and dry conditions. Natural silk is also included for comparison.

Type of Silk	Mean Area of Cross-section of Fibre in sq μ	Tensile Strength in Grammes calculated for 100 sq. μ Cross-sectional Area.		Elasticity per cent. calculated for 100 sq. μ Cross-sectional Area.	
		Dry	Wet.	Dry	Wet
Degummed Italian	109	7 1	6 7	13 2	15 9
Cuprammonium .	105	3 1	2 3	7 9	11 5
Viscose I .	387	3 2	1 8	3 0	2 0
,, II .	596	3 1	1 5	2 3	2 2
,, III. .	498	2 7	1 2	2 8	2 1
Chardonnet T1	584	3 9	2 2	3 5	2 6
,, T2	424	2 7	1 4	3 5	2 4
,, T3 .	728	2 6	1 7	2 6	1 7
,, S, KZ	225	3 3	2 3	3 6	3 2
Acetate	447	1 8	1 5	6 1	5 4

It will be observed that cuprammonium silk is stated to be the only artificial product which resembles the natural product in being more elastic wet than dry.

Both the strength and the water-resisting power of artificial silks are improved by treatment with formaldehyde or other aldehyde, and subsequently heating to 90° or 100° C Thus Karplus (Ger Pat. 382086, 1920, from *J S C.I*, 1924, 90B) adds the aldehyde in solution or in the form of vapour, no other substances being added during the treatment except ammonia or a similar alkali if necessary The treatment may be effected during the manufacture of the fibres, for example, it may be added to the spinning bath or precipitating bath, or both Alternatively, the fibres leaving the precipitating bath may be passed through a bath containing the aldehyde and then heated to a temperature of from 90° to 100° C Artificial silks have the power of taking up considerable quantities of atmospheric moisture Baroni (*J. Soc. Dyers and Col*, 1924, p 123) has made experiments with the different types of silk. Suitable quantities of the silks, after a preliminary exposure of three days under standard conditions in a special chamber, were weighed, then dried at 105° to 110° C., and again weighed to obtain the "absolute weight." They were then exposed under the standard conditions (relative humidity, 65 per cent) and weighed at suitable intervals. The results are expressed in the accompanying table as percentage increases on the absolute weight.

Kind of Silk.	Original Weight	Absolute Weight	Moisture per cent	Moisture per cent after 4 Hours	Moisture per cent. after 6 Hours	Moisture per cent. after 24 Hours.
Chardonnet--						
Mark A	7 857	6 863	14 48	9 57	9 80	12 51
Mark B	7 930	6 952	14 06	9 29	9 42	11 86
Besançon	7 840	6 871	14 10	9 99	10 20	13 09
Vienna	7 910	6 991	13 14	9 24	9 35	11 85
Glanzstoff—						
No 1 .	7 555	6 909	12 24	8 48	8 65	10 88
No 2	7 818	6 980	11 86	8 45	8 57	11 13
Viscose -						
Mark A	7 881	7 019	12 28	8 60	8 77	11 22
Mark B .	7 818	6 976	12 06	8 65	8 83	11 15

CHAPTER X.

MICRO-ORGANISMS AND THEIR ACTION ON COTTON.

All textile fibres are liable to be attacked by bacteria and other micro-organisms, and, as indicated above, this constitutes one of the factors which contribute to the effects of weathering. Before considering the special action of micro-organisms on cotton a brief description of their morphology and natural history must be given.

Micro-organisms may be classified as—

1. Bacteria, including (*a*) cocci and (*b*) bacilli.
2. Moulds (mildew).
3. Yeasts.

All of these are present in the air, soil, and water, and upon all living or dead terrestrial objects.

Bacteria consist of small unbranched vegetable cells, related closely to the lowest algæ and fungi. Each cell consists of protoplasm contained in an envelope (or cell wall), which in many cases is composed of cellulose. They vary in shape from small round cells, called *cocci*, to elongated rod-like forms, termed *bacilli*. Cocci are the smaller forms and have a diameter of approximately 1 μ. Bacilli are many times longer than their width. Thus, for example, *Bacillus subtilis*, a common aerial organism, has a breadth of about 2 μ and a length of 6 μ. A single coccus or bacillus is only visible when viewed under a high-power objective of a microscope. Many can be studied with a $\frac{1}{6}$-inch objective, but more commonly a $\frac{1}{12}$-inch oil-immersion objective is required. Fig. 59 illustrates the difference between cocci and bacilli.

When a bacterium falls upon a fabric it may or may not develop. If it does not, it may either die or remain dormant till conditions favourable to its growth obtain. It then multiplies with enormous rapidity, one bacterium being capable of producing many millions in twenty-four hours. If the growth takes place on a solid medium, the individuals remain in contact and form ultimately a visible spot or patch termed a colony. These may increase in size till adjacent colonies coalesce and a large patch, covered with the bacteria, is produced. When, however, the bacterium gains access to a liquid which will support its growth, the individual organisms remain in suspension and the liquid becomes gradually turbid. Sometimes, also, the organisms will coalesce, forming a skin which floats on the surface.

Bacteria reproduce themselves by two different methods, viz. (1) by fission and (2) by spore formation. The former is the commoner method. A membrane grows across the cell perpendicularly to its length, thus dividing it into two new ones. These then separate and pursue an independent life, repeating very soon the same operation. This is why bacteria multiply so rapidly, the rate being of the nature of a geometrical progression.

Multiplication by spore formation is not met with in every bacterium. Those which adopt this method are always capable of fission also. Spore formation is often made use of, when circumstances are unfavourable to fission, as an alternative process to ensure the continuation of the race. In spore formation a portion of the cell becomes enclosed by a cell wall. The contents of this then become granular in appearance, forming, ultimately, a number of small round bodies termed spores. Each of these contains a portion of the protoplasm of



Bacilli Cocci

FIG 59.

the mother cell, and is surrounded by a thick resistant coat consisting, often, of cellulose The mother cell now disintegrates, thus liberating the spores. These, owing to their resisting coat, are much more difficult to destroy than bacteria. Thus, they are not killed by suspending them in water and bringing it to the boiling-point. Nor are they killed by antiseptics nearly so easily as the bacteria. They may thus remain alive for a long time although they cannot develop till favourable conditions are produced, but when these are, each spore develops rapidly into the organism from which it was produced. Bacilli which produce spores are very persistent *Anthrax* is a good example

Bacteria may be motile. In this case, when suspended in a drop of water and examined under the microscope, they are seen to be in a state of constant movement Their motion may be due to spiral-like movements or to propulsion by means of flagella, which may be seen in fig. 60



FIG 60 — Flagella.

Bacteria produce sometimes white or colourless growths, and at other times coloured colonies. The latter are called "chromogenic." For example, *Bacillus mesentericus* produces a red colour on bread, known as "bleeding bread." They are either (1) strictly aerobic, (2) strictly anaerobic, or (3) facultatively aerobic. The first kind require more or less free oxygen, the second grow in the absence of air, while the third will grow under either condition.

Conditions Necessary for Growth.

The conditions necessary for growth of bacteria are—

1. Moisture.
2. Suitable food material.
3. A certain degree of warmth.
4. The absence of inhibiting substances.
5. A minimum concentration of acid or alkali, *i.e.* a pH value within certain limits.

Moisture is essential. Organisms are not killed by drying at a low temperature, but their growth is entirely inhibited Spores may be kept almost indefinitely in the dry condition without losing their vitality In the case of cotton, Fleming and Thaysen (*J S C I*, 1921, 764A) found that if less than 9 per cent of water was present in cotton the number of micro-organisms did not increase But any increase in the water content above 9 per cent was accompanied by a rapid increase in the number of mirco organisms Thus Indian cotton contains normally 1·4 millions of bacteria per gramme As long as the moisture content did not rise above 9 per cent the number remained the same But with more water, incubation for three days at 16° C produced the following numbers per gramme —

10	per cent	124	millions
15	„	499	„
20	„	1112	„
50	„	9040	„

Food Material.—This must include all the elements necessary to build up protoplasm, viz oxygen, hydrogen, nitrogen, carbon, phosphorus, sulphur, and salts of sodium and potassium Moreover, since bacteria are vegetable organisms, the food material must be soluble in water and diffusible When bacteria grow upon media which do not contain these bodies in a soluble diffusible form, they must first bring about their decomposition into simpler bodies which are both soluble and diffusible They do this by secreting an enzyme which causes the hydrolysis of the complex food into a mixture of simpler bodies Thus, *Bacillus subtilis*, when it grows upon gelatin hydrolyses it into soluble amino salts which it can utilise in the building up of protoplasm As the hydrolysis proceeds, the gelatin becomes gradually liquid Most bacteria can assimulate nitrogen from gelatin or peptone and carbon, hydrogen and oxygen from carbohydrates such as starch, dextrin, or sugar Hence many dressing mixtures form good culture media

Temperature.—Bacteria can only grow between certain limits of temperature As a rule their growth is retarded at low temperatures and inhibited at 0° C But they are not killed at low temperatures They can, particularly if dry, be frozen without being destroyed The maximum temperature of growth is about 98° to 100° F The limits are not the same for all organisms Some which grow at ordinary temperatures do not develop at all at the temperature of the body But, as a general rule, at any temperature up to this maximum the rate of growth increases with the temperature

The Absence of Inhibiting Substances.—Many chemicals retard or inhibit the growth of bacteria These, which are termed antiseptics, will be described later But bacteria themselves, as they grow, produce by products which, when they reach a certain concentration, inhibit the growth of the organism These bodies are termed toxins Pathogenic organisms which produce disease often owe their action to the production of a toxin which, if not destroyed, causes death of the infected animal.

Alkalinity and Acidity -Bacteria can grow either in a neutral, faintly acid or faintly alkaline medium As a rule they grow more readily in an alkaline medium But the pH value of the medium is of more consequence than the actual amount of acid or alkali present Outside certain limits their growth is inhibited

Cotton goods can be infected with bacteria at every stage of the bleaching

and finishing operations. A few of the principal causes may be mentioned (Trotman, *J S.C I*, 1909, p. 1237) These are—

1. The use of impure water for steeping or other operations
2. Incomplete removal of protoplasmic constituents by the lye-boiling process
3. Allowing goods, at any stage, to lie about in a damp condition, especially in warm weather
4. Insufficient cleanliness of plant or buildings.
5. The use of inferior finishing materials, such as low-grade starches and glues.
6. The careless storing of finished goods.

Impure Water -As already mentioned, polluted water always contains a large number of putrefactive organisms and moulds Many of these are able to bring about the liquefaction of gelatin, reducing it to peptones and simpler soluble bodies Their growth is also often accompanied by the production of an unpleasant odour Many organisms found in water, such as *Bacillus subtilis*, are spore-forming and hence difficult to kill. This bacillus is often present in large numbers in cotton yarn, and causes a peculiar and characteristic smell A pure water supply is, therefore, an important consideration. In the initial steeping processes considerable damage may be done by the growth of moulds and other organisms At this stage, owing to the impurities present, rapid growth takes place under favourable conditions, and although pure cellulose alone is not itself a food material, it may, in the presence of impurities, become permanently discoloured or tendered by the action of the by-products of bacterial growth

Incomplete Removal of Protoplasmic Constituents of Cotton —If cotton is completely scoured only traces of nitrogenous bodies will be present, and this scarcity of nitrogenous food makes it difficult for organisms to thrive An imperfectly scoured cotton may, however, contain as much as 0 5 per cent. of nitrogen, or about 3·25 per cent of albuminoid bodies Such cottons are much more readily attacked by moulds and other organisms In nearly all the cases of damage caused by bacterial growth examined by the authors, a high nitrogen content has been found

Careless Handling of Goods —Between the different operations damp goods are sometimes left about in a warm room Moisture and warmth being two essential conditions of bacterial growth, this often results in the development of mould, which necessitates beginning the operations over again. The interval between two successive processes should always be as short as possible, and the leaving of damp goods overnight should always be avoided in warm weather.

Insufficient Cleanliness of Plant and Buildings —Dust and dirt always harbour bacteria, and particularly moulds. Accumulations of dirt should always be avoided, both in plant and buildings; walls and ceilings should be frequently whitewashed

The Use of Unsuitable Finishing Materials —A starch that contains an excess of moisture is likely to be mouldy when used A good starch should never contain more than 10 per cent. of water, but as much as 20 per cent. is sometimes present If such a starch has been stored long, it will frequently contain numerous moulds and other organisms, and the temperature of the finishing mixture will often be insufficient to destroy the spores that are present, thus leaving them free to develop subsequently

Thin starches and dextrins often contain sugar, which is liable to exercise a selective action upon certain moulds or *Torulæ*. Sometimes a starch mixture

goes "sour" before it is used, and if undetected always causes trouble. This is generally aided by the presence of soluble carbohydrates.

Inferior gelatin and glue are sometimes in a similar manner responsible for bacterial growth. The quality of a gelatin depends upon the proportions of true gelatin and peptone present, since the use of poor raw material or faulty manufacture increases the amount of peptone at the expense of the gelatin. Peptones form an ideal germ food, and are also very hygroscopic—that is, they have the power of attracting moisture from the atmosphere. Thus, goods dressed with a gelatin containing peptones will generally be rather damp, and will contain a quantity of ready formed germ food. On this account they are very liable to be attacked by bacteria. One often sees gelatin-dressed goods which have become mouldy and in which the colour has deteriorated; in some cases they even become tender.

Careless Storing of Finished Goods.—Goods frequently leave the bleacher in perfect condition, but subsequently develop a colour. There are, of course, a great many different causes for this, but one of them is undoubtedly bacterial growth, assisted by improper storage. Warehouses should be as dry as possible, and not warmer than is necessary to keep the air dry. Of course, if goods are sent out in a sterile condition, they are not likely to be afterwards attacked if properly stored, but this is, of course, not always practicable All cotton goods contain numberless organisms, and all one can do is to take every precaution that no deleterious organisms are present, and, if so, that the goods are not kept under such conditions as will encourage their growth.

The Effects of Bacterial Growth.—These may become apparent as (1) tenderness owing to the destruction of the cellulose walls of the fibre; (2) discolorations caused by the growth of chromogenic organisms, (3) decomposition of dressing materials, (4) an increased affinity for direct dyestuffs. Micro-organisms destroy cellulose by secreting an enzyme termed "cytase," which changes the insoluble cellulose into soluble dextrose. This is then taken up by the organism, as food, and changed into other simpler bodies, such as carbon dioxide, hydrogen, and organic acids, *e.g* acetic acid and butyric acid. The first stage in the decomposition of cellulose is hydration or swelling up of the cell wall which, like mercerisation, gives the cotton a slightly increased affinity for direct dyestuffs, and may cause uneven dyeings. Thaysen (*J Soc Dyers and Col*, 1924, p. 101) observed that the mycelium of a mould developing on the surface, may pierce the cellulose wall of the hair and penetrate into the lumen. Repeated perforations of the wall naturally reduce the tensile strength, just as the gradual sinking in of large colonies of micro-organisms will do. These are partly the cause of the formation of short fibres, the so-called "fly," which does so much to reduce the value of many cellulose raw materials, and is often the cause of the brittleness of finished fabrics, developed after their exposure to the action of micro-organisms. "Felting" is another manifestation of the action of micro-organisms. It occurs in raw cotton, after having been pressed into bales for transport, and is due to packing the cotton while damp and the consequent growth of micro-organisms. The mycelium of a mould will bind the individual fibres together into hard, felt-like lumps, which sometimes fill the whole of the centre of the bale

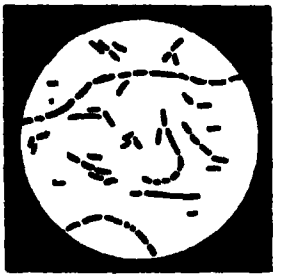
Methods of destroying and preventing Bacterial Growth.—Bacteria may be destroyed by means of dry or moist heat, diffuse sunlight, and chemical reagents.

Heat.—Nearly all vegetative bacteria are killed by exposure for a few minutes to moist steam at 100° C. Spores require much longer, many being able to

withstand this treatment for a considerable time. Their power of resisting dry heat is still greater, some being able to survive a temperature of 140° C. Thus, to ensure the destruction of both bacteria and spores by means of dry heat, a temperature of nearly 150° C. must be employed. Many active organisms, which are instantly killed by steam at 100° C, can withstand the same heat, when dry, for a considerable time. The inhibiting effect of heat is, of course, well known, but it is sometimes forgotten. Finishing mixtures liable to putrefaction should, when possible, be well heated before use to ensure their comparative initial sweetness.

Effect of Light.—Diffuse sunlight has a powerful inhibiting effect on the growth of nearly all bacteria, and in some cases an active toxication If two cultures be made of the same bacterium, and one kept in diffuse sunlight and the other in the dark, it will generally be found that the growth in the latter case is more rapid. Many pathogenic bacteria are killed by exposure to sunlight for several hours The inhibiting power of sunlight is associated with the violet and ultra-violet rays.

Chemical Means of Inhibiting Bacterial Growth.—A great many chemical substances exercise an inhibiting or toxic effect upon bacteria Those which merely inhibit growth are generally termed antiseptics, while those that kill both bacteria and their spores are called disinfectants. There is no definite distinction, however, between the two classes, since many bodies are antiseptics in small and disinfectants in large doses Chlorine is a powerful germicide in the presence of moisture, owing to its ability to decompose water with the liberation of nascent oxygen. It also has a direct toxic effect on protoplasmic matter Since, however, it rapidly becomes changed to hydrochloric acid in contact with water, its effect is not lasting, and it has no permanent antiseptic properties. The same is true of other oxidising agents and of sulphur dioxide, which is a reducing agent, and is oxidised to sulphuric acid. Phenols, salicylic and benzoic acids, being less readily changed, have a more lasting effect. Certain metallic salts, such as copper sulphate, zinc sulphate, and chloride and potassium nitrate, also inhibit bacterial growth



×1000

FIG 61.—*B. subtilis*

For further details of antiseptics see Chapter XXIX.

Bacillus subtilis is a good example of a common aerial bacillus which grows readily on cotton. It is also capable of forming spores. It occurs in air, water, hay, straw, and similar bodies. A culture of this organism can be prepared very easily by heating an infusion of hay and water to a temperature of 80° C. for about ten minutes. This kills all the bacilli present, but not the spores. If the flask containing the infusion be closed with a plug of sterile cotton-wool and kept at a temperature of about 20° C for a couple of days, the spores develop and a culture of the bacillus is obtained. It is a rod-like bacillus with rounded ends, its breadth being about 2 μ and length 6 μ (fig. 61). It is motile, being provided with flagella, by means of which it moves with a wobbling movement through a liquid medium.

Its spores are very resistant, and will withstand, when dry, heating to a temperature of 120° C. for some time without being killed, or boiling water for about one to two minutes. *Bacillus subtilis* grows at any temperature up to 38° C., and causes the liquefaction of gelatin.

Moulds.—These organisms are allied to the fungi, being plants of a very simple structure. If a moist organic substance, such as gelatin or starch paste, be exposed to the air it will frequently become covered with a white or coloured silky growth known as mould or mildew. If a little of the mould is examined under the microscope, it will be seen to consist of a mass of fine filaments, each of which is termed a "hypha." The mass of ramifying and interlaced hyphæ is called a "mycelium" (fig 62).



Fig 62.—*Mucor mucedo*

No division into cells can be observed, the whole being, in fact, a single unit, consisting of a branched filamentous cell containing the cell substance or protoplasm At first the growth is confined to the interlacing hyphæ, or mycelium, but after a time a number of vertical hyphæ are produced, each of which ends in a rounded capsule known as the sporangium The sporangium soon becomes separated from the hyphæ by a transverse partition, and the protoplasm within it granulates and changes into a number of spores, separated from each other by a gelatinous substance capable of absorbing water and swelling. When the spores are ripe the swelling of this gelatinous substance causes the sporangium to burst and scatter the contained spores. Each of these is capable of reproducing the plant in all its stages. In addition to sporulation, moulds also reproduce themselves by a sexual process analogous to that of the higher plants This generally occurs in the absence of a plentiful supply of food material Two short club-shaped hyphæ grow out from adjacent hyphæ till they touch each other In each of these hyphæ a cell wall now appears, cutting off the touching portions from the remainder Next, the cell wall between the two disappears, and the portions of the hyphæ bounded by the first produced cell wall fuse together and form a new cell termed a zygospore This separates from the rest of the plant and under suitable conditions germinates. It becomes ruptured, and an unbranched vertical hypha grows out, at the end of which is formed a sporangium, which bursts when ripe, as already described The different stages in the life of a typical mould (*Mucor mucedo*) are shown in fig 63

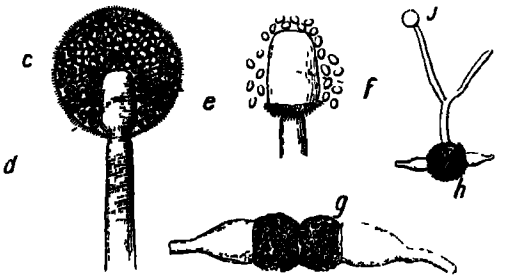


Fig 63.

Although different moulds deviate in details from the common type, their life-history is similar. It is not always possible to identify a particular mould, but any organism which has a life-history like that described is undoubtedly a member of the family.

Yeast.—The yeasts consist of rounded, elliptical cells varying in dimensions with its age and variety, but having approximately a length of from 3 μ to 10 μ. Each cell (fig. 64) has a thick cell wall which consists of cellulose. Within the cell wall is the protoplasm and cell fluid. The protoplasm is more or less granular in appearance, according to the age of the cell, while the cell liquid is, commonly, collected in places into one or more vacuoles. Yeasts are characterised by their power of inducing fermentation. When mixed with a solution of dextrose or levulose, containing small quantities of the other necessary food materials, carbon dioxide is evolved, and alcohol, together with other secondary products, remain in solution This action is due to an enzyme secreted by the cell. Yeast secretes at least three enzymes, viz —

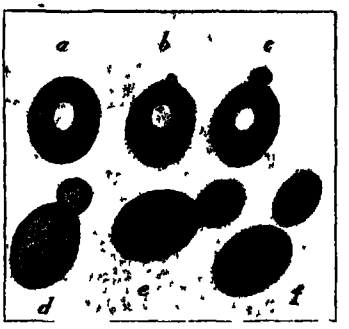


FIG. 64.—Yeast.

1. *Zymase*, which converts dextrose or levulose into alcohol and carbonic acid.

2 *Invertase*, which inverts cane sugar into a mixture of fermentable dextrose and levulose.

3 *Maltase*, which converts maltose into fermentable dextrose.

Yeast reproduces itself, normally, by a process termed "budding." A small end is pushed out at the surface of the cell This grows till it is nearly as large as the mother cell It then detaches itself and becomes a separate individual These stages are seen in fig 64, *b*, *c*, *d*, *e*, *f* In the absence of sufficient food yeast propagates itself, also, by means of spore formation, much the same way as a bacillus

If a smooth block of plaster of Paris, about half an inch in height, be stood with its lower end in water and some yeast be spread on the upper surface, the whole being covered and kept at a temperature of about 25° C, after a few days it will be found that budding has ceased and the cells have changed in appearance. The protoplasm has become granular and is changed gradually into spores, each of which is surrounded by a containing envelope. Ultimately the mother cell disintegrates and the spores are liberated Each spore is capable, under suitable conditions, of producing a yeast cell In addition to the yeasts used in brewing and wine manufacture, there are many varieties of wild yeasts present in the atmosphere These, sometimes, cause the decomposition of dressing mixtures, particularly of those containing starch or sugar.

Torulæ are closely related to yeast. They are, commonly, present in the atmosphere. Like yeast, they consist of round or oval cells which multiply by budding They are often chromogenic Pink and black *Torulæ* are examples. *Torulæ* do not form spores, nor do they, as a rule, produce marked fermentation. Sometimes they produce filamentous threads on the surface of a medium, forming a mycelium similar to that of a mould.

The Action of Micro-organisms on Cotton Cellulose.—Pure cellulose is attacked less readily than that containing protoplasmic residues, which act as food for micro-organisms. Nevertheless, even bleached cotton contains sufficient food for a certain amount of bacterial growth to become possible. In the presence of food, cellulose is decomposed gradually by aerobic bacteria, and this takes place in nature to a considerable extent. There are two views (Groenewege, *J.S.C.I.*, 1921, 76A) as to how this is brought

about. It is either due entirely to aerobic organisms or to two groups of organisms, one of which is aerobic and causes initial decomposition of the cellulose, the other group being denitrifying in action. Groenewege isolated pure cultures of organisms from a culture made from a septic tank liquid and earth, and inoculated a culture medium consisting of tap-water, containing 0·25 per cent. of potassium nitrate, 0·05 per cent. dipotassium phosphate, and 2 per cent. of filter-paper. When this medium was inoculated, either with earth or the septic tank liquid, and incubated at 37° C, gas was given off, the nitrate reduced to nitrite and nitric oxide and the paper to a pulp If, at this stage, the solution were poured off from the pulp and more of the medium, but without filter-paper, added, reduction of nitrate again took place and the pulp was dissolved gradually. The organisms in these cultures were subcultured on agar plates and pure cultures obtained They were found to fall into three groups, viz —

1. Those which effect denitrification but do not attack cellulose
2 Those which attack cellulose but have no denitrifying action
3 Those which have no denitrifying action and do not attack cellulose.

The first group contained such organisms as *Bacillus vulgatus* and *B opalescens*, while the second contained *B cellaresolvens*. He concluded that the different varieties of the last-named organism attack cellulose, and that the decomposition products serve as food for the denitrifying organisms *B viscosus* and *B. opalescens*. The end products are acetic, butyric, and lactic acids, which are oxidised to carbon dioxide and water by the nitrifying organisms It is suggested that the initial decomposition of the cellulose is due to an enzyme cellulase

Hutchinson and Clayton (*J S C.I.*, 1919, 381A) inoculated Rothamsted soil into mineral culture solutions containing filter-paper, and isolated an organism which they named *Spirochæta cytophaga*, which attacked cellulose very readily It grows best in a solution of nutritive salts, such as nitrates, ammonium salts, amides and amino acids, at low concentration All carbonaceous substances, except cellulose, inhibit its growth, but cellulose in any form is rapidly decomposed at 25° to 30° C., producing a mucilage with a pectin-like character

Clark and Scales (*J.S.C.I*, 1916, p 480) observed, also, that *Penicillium pinophilum*, which occurs in soil, is one of the most active destroyers of cellulose. Cultures grown in a solution containing ammonium sulphate or peptone, as a source of nitrogen, reduced filter-paper to a soft pulpy condition in about two weeks. Many enzymes were separated from the cultures.

It is obvious that even purified cotton is liable to be attacked by micro-organisms. Impure cotton, or dressed goods, offer still more favourable conditions for their growth Dorée (*J S.C.I*, 1921, 342A) found that the organisms of sea-water had a destructive action on cotton, causing its complete disintegration in about three weeks

Fleming and Thaysen (*loc cit.*) have made important contributions to the knowledge of the action of bacteria on cotton. They investigated chiefly the fact that exposure to damp air renders cotton brittle and short fibred. This increases its solubility in alkali, causing sometimes a loss of from 10 to 15 per cent. It has been mentioned above that they found that, for this to occur, a moisture content of not less than 9 per cent. was necessary, together with the fact that cotton contains normally 1·4 millions of micro-organisms per gramme.

They found that these included both moulds and bacteria, the latter consisting largely of *Streptothrix*. In the case of cotton exposed for five days to the action of damp air, 2,300,000 *B subtilis* and some *B. fluorescens* were found. The effect of this growth is to cause perforation of the cuticle, and this they attribute to attack by *Streptothrix*. When the cuticle has become perforated, the fibre acts abnormally when treated with swelling agents. It does not give the characteristic globular swellings and ruptured cuticle forming rings round the hair (fig 26), but swells up uniformly, no globular swellings being seen They arrived at the following conclusions, and indicated also a method of testing for bacterial damage :—

The presence of a very large number of micro-organisms in raw cotton indicates that the cotton has been exposed to damp. The presence of a smaller number (up to a few millions per gramme) of organisms is due to a contamination of the cotton during the various stages of growth and preparation. For the quantitative determination of the bacterial deterioration of cotton, about 0·2 gramme of a representative sample of the cotton is treated with 1·5 grammes of carbon bisulphide and 1·5 grammes of 15 per cent sodium-hydroxide solution [illegible] minutes or [illegible] when the optimum swelling has been attained, the sample is thoroughly [illegible] and about twenty fibres are removed and placed on a microscope slide, [illegible] added, and a drop of water allowed to diffuse into the slide ; the number of fibres which under the microscope appear to be attacked along their whole length gives an accurate measure of the percentage of decomposed fibres present The results are more reliable than those of the alkali solubility test.

Thaysen and Bunker (*J Text. Inst*, 1924, 117A) have shown, by means of the swelling test, that raw cottons of different origin vary in their resistance to destruction by micro-organisms This resistance is due, probably, to difference in the physical or chemical nature of the respective hairs. Since the resistance disappears when resistant strains are cultivated in a country producing a non-resisting type, it is concluded that the resistance is affected adversely by climatic or soil conditions Destruction of Indian cottons takes place more rapidly than those of American or Egyptian origin.

It should be noted, however, that Denham (*J Text. Inst*, 1922, T 240) criticises this test. He is of opinion that examination of the cuticle is not altogether reliable, and that the test described by Fleming and Thaysen takes no notice of the organisms which may grow in the cell walls and lumen of the hair, and which often cause damage even before structural alteration can be observed

Having regard to Fleming and Thaysen's observation of the number of *B. subtilis* organisms found on cotton after exposure to damp air, the following experiments (Trotman and Sutton, *J.S.C.I.*, 1924, T. 190) may be referred to, although Thaysen was unable to confirm the results obtained —

When cotton is incubated with a culture of *B subtilis*, the first effect observed is a swelling up of the cell walls and loss of natural twist. This is accompanied by the formation of occasional globular swellings (fig. 65) which sometimes cause rupture of the cuticle (fig. 66) These swellings are not identical with those described by Denham (*J. Text. Inst*, 1923, T. 85), since they were not found in the original cotton The tensile strength, in the case of cotton yarns, increased slightly at first, reaching a maximum in three days. After this it decreased, becoming less than that of the original cotton. The water content was in all cases the same when the samples were tested.

The following table illustrates the rise and fall in tensile strength :—

Time of Incubation	Tensile Strength.
Original cotton .	15 0
After 24 hours .	15 4
„ 48 „ . . .	16·5
„ 96 „ .	18 4
„ 7 days . .	12·0

The swelling is accompanied by a slight decrease in length. The tensile strength increases as the swelling proceeds, till the globular formations become marked. Loss of tensile strength seems to become apparent when the globular swellings are evident. The incubated cotton appears also to have a slightly

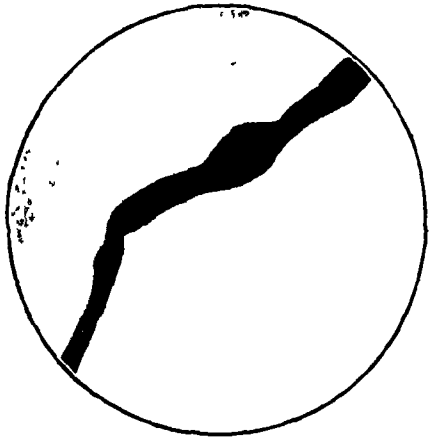


FIG 65.—Action of *B. subtilis* on cotton

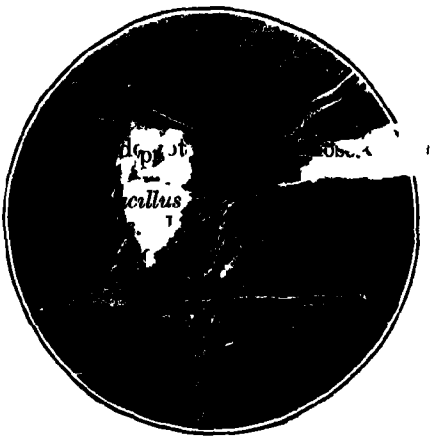


FIG 66.—Action of *B subtilis* on cotton.

increased affinity for benzo-purpurin. These points are summarised in the following table Six lots of Egyptian cotton yarn, each exactly 60 yards in length, were inoculated with a culture of *B. subtilis* and incubated at 37·5° C One lot was removed at the end of each three days, washed and examined At the end of the experiment the samples, together with a control, were wetted with water and allowed to dry at room temperature for several days, to ensure the same " condition " with regard to moisture.

No Experiment	Duration of Experiment	Length.	Tensile Strength.	Microscopic Appearance
0	blank	60 yds	1 30	
1	4 days	60 „	1 34	Fibres swollen with little twist
2	7 „	60 „	1 43	„ „ „ „
3	10 „	59 yds 23 ins	1 45	„ „ „ „
4	13 „	59 „ 25 „	0 95	Increase in damage
5	16 „	59 „ 25 „	0 97	„ „ „
6	19 „	59 „ 2 „	1·00	„ „ „

Samples Nos. 4, 5, and 6 contained more of the globular swellings than the

earlier ones, and it will be noticed that this point corresponds with the decrease in tensile strength. In all cases Schweitzer reagent gave very few characteristic globular swellings.

The action of *B. mesentericus* was tested in a similar manner. The results were the same, but the action was less marked. A similar swelling of the fibres was observed, together with the formation of occasional globular swellings. The swelling is also accompanied by an initial increase in tensile strength, rising to a maximum and then gradually falling After four days' incubation, in one example the tensile strength increased from 9·66 to 10·88 and a small but distinct increased affinity for benzo-purpurin was noticed Prolonged incubation gradually produced a tensile strength below that of the original, as with *B subtilis*

Corrigan (*J Soc. Dyers and Col.*, 1920, p. 198) found that cotton can be attacked by both aerobic and anaerobic bacteria.

Moulds or mildew cause both discolorations and destruction of the cotton hair, and are the cause of much trouble. Considerable attention has been given to the study of this part of the subject. The present authors (*J S.C.I*, 1909, p 1237) have investigated many cases of damage traceable to the growth of mould The following is an illustration :—

A number of pieces of white lace left the finisher apparently in perfect condition, but were subsequently returned on account of their having developed a pink colour The colour was so evenly distributed that the goods appeared to be dyed, and the most obvious suggestion was that they had been accidentally finished with some coloured goods A microscopic examination showed the presence of numerous very fine hyphæ interlaced with the cotton fibres, and subsequent plate cultures upon a starch medium similar to the dress used for the lace proved the presence of a chromogenic mould, which was capable of producing the observed pink colour The point was conclusively proved by infecting sound lace with the organisms. An interesting point in connection with it was, that it required the presence of a little acid to readily develop its colour, and the dress in question was actually prepared with a small proportion of tartaric acid Careful examination of the circumstances under which it was bleached proved that the infection was aerial, and occurred while the goods were lying about after the soda boil The subsequent operations were not sufficiently drastic to destroy the spores present, and, on storing, they developed with the astonishing results described The fact that at least a fortnight seemed to be necessary for the development of the colour explained the goods being passed when finished

Osborn (*J S C I*, 1912, p 636) observed that "mildew" in cotton was due to both bacteria and moulds. Among these he identified *B. megatherium*, *sarcina*, *aurantiaca*, *Penicillium glaucum*, and *Mucor racemosus*. He noted also that a certain degree of moisture was essential to growth.

Levine and Veitch (*J. Soc Dyers and Col.*, 1920, p 119) thought that mildew was caused chiefly by such moulds as *Alternaria*, *Cladosporium*, and some *Mucors*.

Sidebotham (*J. Soc Dyers and Col*, 1922, p 97) traces discolorations to a mould termed *botrytis*, whilst Broughton and Alcock (*J. Soc. Dyers and Col.*, 1923, p 307) think that the chief agents in the case of cotton canvas are fungi of the genera *Macrosporium* and *Stemphylium*.

The following details concerning moulds are taken from a paper by Bright, Morris, and Summers (*J. Text. Inst*, 1924, T. 547).

The frequency with which such cases of damage are reported shows that attack by mildew is a serious source of trouble in the cotton industry. As a rule moulds will grow slowly at temperatures of about 7° C., but rise of temperature causes rapid increase of growth till an optimum temperature is reached,

beyond which further increase causes a decrease in growth, and finally the maximum temperature is reached, beyond which no growth is possible.

Name of Mildew	Optimum Temperature	Maximum Temperature
Aspergillus (black) .	37° C.	43° C.
„ (white) . . .	25° C.	37° C.
Penicillium . .	27° C	39° C.

The presence of sufficient water is also essential if the mildew is to grow, and it has been found that growth is possible on a fabric with a moisture content of 8 per cent, but is most vigorous when the moisture is between 10·6 and 13 6 per cent During spinning the temperatures are usually between 21° and 27° C., precisely those which are most favourable for growth Whilst certain moulds require starchy substances, supplied in the size, for food, others such as *Chætomium* can attack the pure cellulose

Very frequently the raw cotton itself is infected, though, of course, it is always liable to subsequent infection The processes of bleaching and mercerising would kill any mildew or spores already present, so that such goods, when attacked, must have been infected after they had been subjected to the above processes In the early stages the fungus grows round the outside of each fibre, like ivy round a tree, but at a later stage it penetrates the fibre and the hyphæ may be seen running down the central cavity The growth of moulds is invariably accompanied by considerable tendering of the yarn The most striking effects of the action of mildew are seen on dyed goods. In the first place, cotton which has been attacked has an increased affinity for dyes, and secondly, the products of mould activity are either of an acid or an alkaline nature, and may therefore produce marked changes in the colour of the dye

The prevention and control of mildew naturally requires a suitable antiseptic, but up to the present their application has not been very successful Zinc chloride has been used, but it causes harshness, and further, it has been found that fabrics so treated are still liable to attack by mildews Other antiseptics which have been recommended are phenol and salicylic acid, but experiments have shown that neither of these compounds successfully fulfil their object. The best prevention that can be recommended is the spreading of methods of cleanliness It has also been found that "nepping" cotton is much more liable to attack owing to the nutritive materials contained in the particles of seed coat. Soaking infected fabrics in weak formaldehyde solution for twenty-four hours will effectively kill all the mildew, but this compound cannot be applied as an antiseptic in size owing to its hardening effect on starch pastes Prolonged boiling or steaming will sterilise the goods, but will not protect them against future infection The composition of the size is also of importance, for it has been found that farina, sago, and tapioca are least liable to infection, whilst wheat is most liable of all, and rice and cassava are only slightly less readily attacked Finally, if mildew is to be prevented, every precaution must be taken to avoid excessive moisture

Regarding the susceptibility of fabrics to develop mildew, Reiners (*J. Text. Inst*, 1924, 117A) states that on fabrics of low moisture content, *Aspergillus niger* and *Aspergillus glaucus* moulds are likely to develop first, while white, yellow, and brown *Aspergillus* may also appear. A slightly higher moisture

content is favourable to the common green mould *Penicillium glaucum*. *Mucor* moulds require also a high humidity. Cotton itself contains all the ingredients necessary for the propagation of mildew, though they are not so accessible as those in starch-sizing mixtures. All moulds secrete enzymes capable of destroying cotton.

Enzymes.—It has been stated that when micro-organisms decompose textile fabrics or dressing materials, they do so by the aid of an enzyme or ferment. The process of the production of alcohol, from solutions containing sugar, by means of yeast is one of the most important examples of enzyme action. Yeast produces several different enzymes. The chief of these are—

1. *Zymase*, which converts dextrose or levulose into alcohol and carbon dioxide—

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

2. *Invertase*, which changes cane sugar into dextrose and levulose—

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

3. *Maltase*, which changes maltose into dextrose—

$$C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6.$$

Other micro-organisms produce the same or different enzymes Acetic, lactic, and butyric acids are all formed in a similar manner, by enzymes produced by particular micro-organisms. Others contain enzymes capable of liquefying starch or proteins, or of bringing about the decomposition of cellulose.

There are enzymes, also, which are not produced only by bacteria, although acting in a similar manner. Malt, for example, contains "diastase," which is able to convert starch into a mixture of dextrose and dextrin Enzymes are, in fact, contained in most vegetable tissues Others are of animal origin. The saliva, gastric, and pancreatic secretions of animals all owe their action to the presence of enzymes

Ferments or enzymes are of two kinds, viz.—

1. "Organised ferments" or enzymes, which are associated with living cells.
2. "Unorganised ferments" which are not necessarily connected with the presence of living cells, but can induce chemical change in a sterile medium

The Nature of Enzymes.—Enzymes are colloidal organic substances which give the general reactions of proteins, but which contain, also, a small proportion of mineral matter. Their constitution is unknown, since they cannot be prepared in a pure state. They must, however, have a large molecular weight. They are soluble in water, but are, as a rule, precipitated by the addition to their solutions of alcohol, sodium, or ammonium sulphate. They are also carried down by such bodies as calcium phosphate when precipitated in their presence. Enzymes can be prepared by extracting tissues or organisms containing them with water or dilute glycerol, concentrating the solution at a low temperature and adding a large excess of alcohol The precipitate thus obtained is extracted with water and reprecipitated with alcohol. This precipitate is once more extracted with water, and the solution obtained is purified by dialysis and again precipitated by alcohol.

Wood (*J.S.C.I.*, 1918, T. 313) prepared enzymes by taking advantage of the fact that cellulose adsorbs an impure mixture of protein and enzyme, and that, after drying, the colloidal protein portion adheres firmly to the paper, whereas the enzyme is readily soluble. "Ordinary circles of Swedish filter-

paper (12½ cm. diameter, ash 0·0095 gramme, weight when dried in air 0·87 gramme) are soaked in the impure enzyme solution and dried quickly in a current of hot air. When the dried paper is placed in water the enzyme dissolves, quickly forming a perfectly clear solution in a few minutes, whilst the colloidal matter with which it is associated adheres firmly to the paper. After twenty minutes' soaking the solution is filtered. The whole of the enzymes are in the filtrate."

General Properties of Enzymes.—Enzymes are white or colourless amorphous substances, with well-marked colloidal properties. They act in a manner similar to that of ordinary inorganic catalytic agents, *i e* they induce chemical change without being themselves apparently altered. The chemical changes brought about by the action of enzymes are generally of the nature of hydrolysis. Their action resembles closely that of acids. For example, the decomposition of starch by means of a dilute acid and by diastase are of exactly the same nature, namely, hydrolysis, neither the acid nor the diastase being altered. The action of an enzyme differs from that of an ordinary catalytic agent in an important particular. The ferment cannot induce chemical change indefinitely. It is destroyed gradually, during the process, either by ordinary wear and tear or by the temperature or the products of the reaction. Any given quantity of an enzyme can only induce a certain amount of chemical change, while in the case of the common catalytic agents no such limit is fixed. Enzymes act only under certain definite conditions, which vary with the kind of enzyme. Temperature is an important factor. As a general rule the enzyme is only active between certain limits. They are generally inactive at the freezing-point. Their activity increases gradually with rise of temperature till a maximum is reached. Above this their action becomes gradually less, till a limiting temperature is reached, at which they are destroyed. When once destroyed by heat their activity cannot be restored by cooling. Animal enzymes act best, as a rule, at the temperature of the body, *i e* about 37° C. Vegetable enzymes often are more active at a lower temperature, about 25° C., though diastase of malt is most active at 65° C. Temperatures above 65° C. cause restricted action, while at from 80° to 100° C. all enzymes are destroyed.

As a rule enzymes act best in a neutral or faintly acid solution, but there are exceptions. Trypsin, the proteolytic ferment of the pancreas, acts best in faintly alkaline solutions containing about 0·05 per cent. of sodium carbonate, and can work up also in concentrations up to 2 per cent. Pepsin, on the other hand, is most active in a solution containing 0·2 per cent. of hydrochloric acid. Trypsin is destroyed by acids and pepsin by alkalis. As a rule there are definite pH values between which a particular enzyme can act.

Enzyme action is not inhibited by many bodies which inhibit bacterial growth, such as thymol, chloroform, fluorides, etc., but large additions of any foreign substance restrict or inhibit their action. Small quantities of neutral salts are, however, frequently advantageous. Thus, it is claimed that the presence of neutral salts renders animal amylases much less sensitive to changes of temperature, and also the diastatic enzymes produced by such organisms as *B. subtilis* or *B. mesentericus*.

Enzymes bring about three kinds of reactions (Cohen, *Organic Chemistry*, vol. iii. p. 70), viz.—

1. Simple hydrolysis.
2. Oxidations and reductions.
3. Induce clotting of certain substances.

1. **Hydrolytic Enzymes.**—Among the more common enzymes which induce hydrolysis are—

(a) *Diastase*, which is present in many plants, bacteria, moulds, and germinating grain. It converts starch into varying mixtures of maltose and dextrin.

(b) *Cellulase* (or cytase), produced by many bacteria, moulds, and vegetable tissues. It hydrolyses cellulose into soluble products, such as reducing sugars

(c) *Pectase*, a vegetable enzyme which is concerned in the hydrolysis of pectose into pectin and pectic acid.

(d) *Lipase*, which is found in castor oil and other seeds, and which hydrolyses triglycerides into glycerol and fatty acids

(e) *Emulsin*, a vegetable enzyme present in bitter almonds and other plant tissues. It hydrolyses the glucoside amygdalin into glucose and hydrocyanic acid.

(f) *Trypsin and pepsin*, the enzymes of pancreatic and gastric juices respectively, which hydrolyse proteids into peptones, polypeptones, and, ultimately, into amino acids.

2 **Oxidases and Reductases.**—The oxidation of alcohol to aldehyde and acetic acid is brought about by an enzyme produced by the *Bacillus aceti*. Another oxidising enzyme present in malt extract is catalase Its use has been suggested for increasing the activity of bleaching solutions Many bacteria are able to reduce sulphates to sulphuretted hydrogen owing to the production of a reducing enzyme or reductase.

3 **Clotting Enzymes.**— When blood is allowed to stand for some time it clots. This is caused by a "clotting ferment" termed thrombase In a somewhat similar manner milk is clotted by the enzyme rennin.

CHAPTER XI.

WATER.

Of all bodies used in bleaching, water is by far the most important, since it enters into every stage of the operations, either as a vehicle for the chemicals used, or as a solvent for the impurities which have to be removed. The difference between the results obtained by two different bleachers is very often due to the differing composition of the water used.

In selecting a site for a bleach-works, the first thing to be considered is, of course, the quantity of available water; but, too often, if the quantity is sufficient, no very searching inquiry is made into its quality Yet quality is of even more importance than quantity, since an unsuitable water may make it very difficult to obtain the pure white colour demanded for fine goods, while the loss of soap occasioned by hardness and the trouble caused by calcium soaps in the goods, or scaling or corrosion of boilers, may cause not only difficulties in working but considerable financial loss. Whether water is used for steam-raising or as a solvent, the nearer it approaches to theoretical purity the better will be the results obtained

Since, however, pure water is rarely obtainable, it is necessary that one should have some accurate knowledge of the impurities which are likely to be met with, and of the effects they will have in practice

Water occurs in nature in three different forms, viz . (1) Water-vapour, (2) liquid water, and (3) ice or snow. All living organisms are composed largely of water Living animal tissues, such as muscle, contain about 70 per cent., ordinary terrestrial plants from 70 to 75 per cent, and aquatic plants from 90 to 95 per cent. Many minerals contain either mechanically retained or chemically combined water Gypsum, for example, has the formula $CaSO_4\,2H_2O$. Natural water must be continually passing through a cycle of changes in order that it may be available for the support of animal and vegetable life This cycle starts and ends with the sea It is of the following nature. The heat of the sun causes the evaporation of water from the surface of the ocean (and also from that of lakes and other exposed surfaces), forming water-vapour Water-vapour, being lighter than air, tends to rise and become diffused into the upper atmosphere. As it rises, both it and the air become colder.

Now, the quantity of water-vapour which the atmosphere can hold depends upon the temperature, other conditions remaining constant Warm air can retain more water-vapour than cold air Thus, a point will be reached when the water-vapour present is sufficient to saturate the air. The water-vapour then becomes condensed into very fine liquid particles, forming mist or clouds. Any further cooling causes these particles to coalesce into drops of water, which fall to the earth in the form of rain, snow, or hail. When this reaches the earth, it is taken up, partly, by the leaves and roots of plants, from the leaves of which it is again lost by evaporation The remainder either trickles over the surface

of the earth, forming streams, pools, or lakes, from which it ultimately reaches the sea, or sinks into the earth, forming the subterranean supply which is tapped by wells.

Classification of Water Supplies.—Natural waters may be classified as follows:—

1. Rain water, including all water derived directly from the atmosphere.
2. Surface water, that is, rain water which has collected in natural reservoirs such as lakes, streams, etc.
3. Subsoil water, or water which has percolated into the subsoil and collected in the uppermost water-bearing strata below the surface. This class includes all shallow wells
4. Deep well water, or water obtained from the deeper water-bearing strata, which are protected from the subsoil water by an impermeable stratum. These waters have generally travelled a long way through the earth, during which time natural purification has taken place

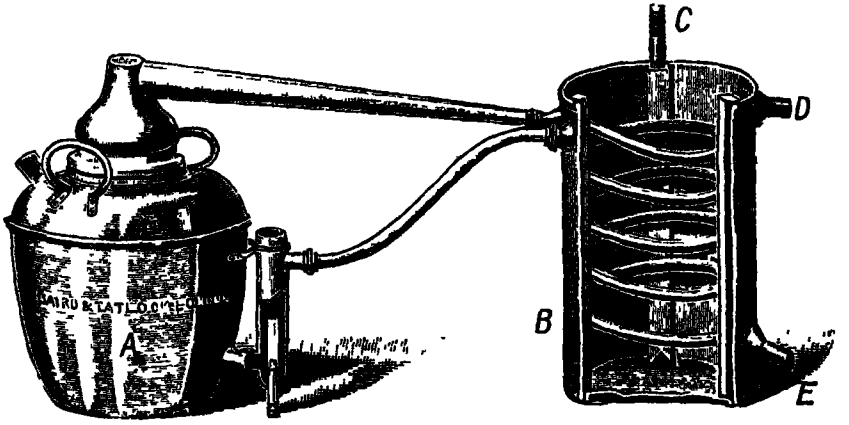


Fig. 67.—Distilled water apparatus

Distilled or condensed water is, if made carefully, practically pure water, containing only dissolved gases It is made by boiling natural water and leading the steam or water-vapour through a condenser Fig 67 illustrates an apparatus which may be used for this purpose The water is placed in the copper vessel A, which is connected to a condensing worm surrounded by cold water in the container B. Cold water flows in at C and leaves at D. The condensed water-vapour runs out of the condensing worm at E. The dissolved salts and solid impurities remain in the boiler A, but dissolved gases are expelled and redissolve in the condensed water It may be expelled by boiling the distilled water and cooling it out of contact with air.

Distilled water, generally termed "condensed" water, is often made in works by condensing steam from a boiler. It may contain dissolved salts owing to frothing or priming, in the boiler, which results in the carrying over of some of the water with the steam

Properties of Water.—Pure water is a tasteless, odourless liquid and, when viewed in a thin layer, colourless In thick layers it appears to have a greenish or bluish tint It is a comparatively poor conductor of heat For example, if a test-tube be nearly filled with water and the upper portion held in a Bunsen flame, the water at the top of the tube may be boiled while that lower down

remains comparatively cool. When the bottom of the tube is heated the water, as it becomes hot, expands, and becomes lighter than the colder portions. Consequently it rises, and the heavier colder water takes its place, becoming in its turn heated. In this way a constant current (termed a convection current) is produced, which enables the whole mass to become heated. The heating of large quantities is for the same reason facilitated by keeping it in a state of gentle motion

As the water is heated it gives off water-vapour, until a temperature is reached at which the pressure of the water-vapour is equal to that of the atmosphere. Ebullition then commences For the normal atmospheric pressure of 760 mm this occurs at 100° C If the pressure be increased, the boiling-point rises, while if it be decreased, it falls proportionately. That is, the boiling-point varies with the atmospheric pressure. At the summit of Mt Everest the boiling-point is about 72° C In fact, the altitude may be determined by noting the temperature at which water boils On the other hand, if the pressure be increased to 2 atmospheres, the boiling-point is raised to 120° C When water boils, an invisible vapour is produced But when this comes into contact with air, as is the case when it issues from the spout of a kettle, it becomes condensed into a cloud of minute particles of water known as steam. In order to convert water at 100° C. into water-vapour at the same temperature a considerable quantity of heat must be supplied The amount of heat necessary to convert 1 gramme of water at 100° C into vapour at the same temperature is 537 calories This quantity is termed the "latent heat" of vaporisation. When water-vapour at 100° C is reconverted into liquid water at the same temperature, this latent heat is given up This is why cold water can be heated or boiled by passing steam into it. When water is cooled to 0° C, it freezes or becomes changed into the solid state As it solidifies it expands, so that the ice is lighter than the volume of water from which it was produced Hence it floats on the surface At the same time heat is liberated to the extent of 80 calories for each gramme of ice Conversely when ice at 0° C melts to water at the same temperature, 80 calories of heat must be supplied from its surroundings This is why ice is used to reduce the temperature of liquids. When water is cooled it contracts and becomes heavier, sinking to the botton of the containing vessel, the warmer layers underneath rising to be cooled in turn But water at 4° C is heavier than at 0° C Hence when the surface of a lake is frozen, there is always a stratum of water underneath which does not fall below 4° C., and circulation ceases This prevents the whole of the water in the lake from becoming changed into ice, and provides a moderately warm layer in which fish can remain with security.

Water is comparatively incompressible If 1000 c c. of water are subjected to a pressure of 2 atmospheres the decrease in volume is only 0·05 c c

The most important property of water is its power of dissolving other bodies. All gases, and many liquids and solids, are more or less readily dissolved It is to this property that water owes its use in bleaching. Different substances dissolve to differing extents, and some hardly at all It is doubtful whether any substance is really absolutely insoluble in water. Bodies may be classified as (1) readily soluble, (2) moderately soluble, or (3) sparingly soluble (or insoluble). But water can only dissolve a definite quantity of any particular substance. If 100 c.c. of water at 0° C are shaken with excess of any soluble substance or salt, till the water has dissolved as much as possible, the solution obtained is said to be "saturated," and the weight of the salt which is dissolved is termed its "solubility" at 0° C As a rule, the solubility increases with the temperature

up to 100° C., though in a few cases less is dissolved at the boiling-point than at 0° C. The following table contains some examples —

	Solubility		
	0° C.	50° C.	100° C
Potassium nitrate . .	13 0	86 0	247 0
Sodium chloride . .	35 6	36 6	39·1
Calcium hydroxide . .	0 14	0 10	0 06

When a hot saturated solution of a soluble salt is cooled, or when a solution which is not saturated is concentrated, it can no longer retain in solution the whole of the dissolved salt The excess, above that necessary to keep the solution saturated, is deposited in the form of crystals. These crystals have a definite crystalline structure and contain, often, water in combination, termed water of crystallisation Thus .

Copper sulphate	$CuSO_4\ 5H_2O$
Magnesium sulphate	$MgSO_4\ 7H_2O$
Alum	$Al_2(SO_4)_3(NH_4)_2SO_4\ 24H_2O$

Sometimes, when a solution of a crystalline salt is cooled to its saturation-point, it does not crystallise and is said to be " supersaturated " When a hot saturated solution of sodium sulphate is cooled, in a perfectly clean flask, plugged with cotton-wool to prevent entrance of dust, and without agitation, it remains liquid This supersaturated solution may be kept almost indefinitely. But if a minute crystal of sodium sulphate be dropped into the flask, it immediately crystallises, forming a solid mass. An aqueous solution of a soluble salt may be either unsaturated, saturated, or supersaturated. Which it is may be determined by adding a crystal of the salt If the solution be unsaturated, the crystal will dissolve; if saturated, it remains undissolved, while if supersaturated, rapid crystallisation immediately occurs.

The Impurities of Water.—Owing to its great solvent action natural waters always contain dissolved saline and other substances.

The impurities may be either—

1. In suspension.
2. In solution.

The suspended impurities include dirt, mineral matter, vegetable or animal debris, and micro-organisms, such as moulds and bacteria.

The chief dissolved impurities are the gases of the atmosphere, the soluble products of decaying organic matter, soluble salts such as sodium chloride, and compounds of calcium and magnesium When animal or vegetable matter becomes decomposed, soluble compounds containing nitrogen are produced. These may be either salts of ammonium, which are readily decomposed when boiled with an alkali, or more complex compounds which only give up ammonia when heated with an alkaline solution of potassium permanganate. Both kinds of compounds are estimated in water by means of the ammonia which they yield. This ammonia is termed (1) saline ammonia and (2) albuminoid (or protein) ammonia. When nitrogenous organic matter is exposed to the action

of oxygen and nitrifying bacteria, it is changed ultimately into nitrates. Hence albuminoid or protein ammonia, saline ammonia, and nitrates all indicate nitrogenous organic matter in different states of decomposition.

Salts of calcium and magnesium constitute "hardness," a term which will be described fully later.

Rain Water.—The water most nearly approaching purity is rain water, and, if properly collected and available in sufficient quantity, there is no better supply. It always contains dissolved oxygen and atmospheric carbon dioxide, as well as nitrogen. Traces of ozone and hydrogen peroxide are also frequently present. In the neighbourhood of towns it brings down with it other dissolved and suspended impurities, such as soot, sulphuric acid, putrefying moulds, and bacteria. Hence it is only in open country districts that it can be used without treatment. Rain water can be freed from its suspended impurities by careful filtration through sand beds

A satisfactory filter may be made by filling a small tank with alternate layers of pebbles and fine sand, commencing at the bottom with the coarser material Or the bottom of the tank may be covered with pebbles to a depth of 1 or 2 feet, and this, in turn, covered with sand The sand must be renewed at intervals. The total depth of the filter bed need not exceed 3 feet Alternating layers of gravel and sand give more rapid filtration

Carefully collected rain water has approximately the following composition —

	Parts per 100,000
Total solids	3 00 to 5 00
Chlorine as chlorides	0 006 ,, 1 00
Nitrogen as nitrate	0 005 ,, 0 025
Free ammonia	traces ,, 0 025
Albuminoid ammonia	traces ,, 0 025
Hardness	nil.

The best results in bleaching are obtained with surface waters approaching rain water in composition By making use of a proper storage tank and adopting a suitable method of collection, it is often possible to obtain a fairly good supply of rain water With an average rainfall of from 15 to 18 inches, about 30 gallons per day can be collected from 100 square yards of collecting surface. Although this is not a large quantity, it would be sufficient for some of the finer and more delicate operations of bleaching. In collecting rain water the following precautions must be observed —

1. The collecting tank must be of sufficient size

2 If collected from a roof, some method must be adopted by which the first portions are rejected, since these will always contain dirt and other matter which should not be allowed to enter the storage tank.

3 There must be an efficient filter.

The first portions of a rainfall may be rejected by means of a Roberts' Rain Water Separator (Thresh, *Water Supplies*, p. 23), which rejects the dirty water, allowing only clean water to enter the tank It contains a canter which is balanced upon a pivot. When the canter is full it overturns and discharges its contents into a waste pipe, after which the water is directed into the storage tank Collection from a roof may be largely supplemented by selecting a suitable piece of sloping ground and making its surface impervious to water by means of cement. Thus it has been calculated that if half an acre of land were treated in this way, about 170,000 gallons of water could easily be collected during the six winter months of the year.

Storage tanks for rain water should be lined with cement or other material

insoluble in water. The effect of careless collection and storing is seen in the following figures in the case of rain water collected from a foul roof and stored in a tank the lining of which was not insoluble:—

	Parts per 100,000.
Total solids	22 00
Chlorine as chloride .	1 42
Free ammonia .	0 042
Albuminoid ammonia .	0 053
Hardness . . .	16 50

Surface Water.—When rain falls on the earth, part of it sinks into and percolates through the soil. The remainder trickles away over the surface, becoming collected, ultimately, in natural reservoirs such as brooks, rivers, ponds, and lakes. Such water is known as surface water. As it flows over the land, it carries with it organic matter in various stages of decomposition, in suspension and solution, and, also, more or less saline matter depending on the nature of the soil over which it flows and the slope of the watershed. When the water reaches its natural reservoir, it deposits most of the suspended matter but retains its dissolved organic or inorganic constituents The dissolved organic matter is, however, rapidly attacked by nitrifying bacteria in the presence of oxygen with the formation of nitrates. Thus, unless directly polluted by sewage matter, these waters are, as a rule, organically pure They often receive considerable additions of dissolved saline bodies from shallow springs, bringing in water which has travelled for some distance through the earth. Surface water has occasionally a distinct colour, derived from the soil over which it has passed, and is generally highly charged with dissolved oxygen. The character of surface water is variable. Where the surface is hard, impervious, and unable to support vegetation, the water runs off quickly and contains but little dissolved matter. When the rocks have become disintegrated by weather a certain amount of soluble matter is given up and the debris becomes able to support vegetable life. In this way both organic and inorganic impurities are introduced into the water Where the surface is covered with decaying vegetable matter, such as peat, a large amount of organic impurity may be present in the water The following types of surface waters of England and Wales are given by Thresh in his book on *Water Supplies*, p. 29:—

1 Water from igneous rocks, such as those of Devon and Cornwall, yielding very little inorganic matter, but frequently, owing to the presence of peat, considerable quantities of organic impurities They contain very little lime.

2. Water from the Metamorphic, Cambrian, Silurian, and Devonian rocks, giving water very similar to that from igneous rocks. Most of these rocks are very hard and almost impervious. They are found in Wales, Westmoreland, Cumberland, Devon, and Cornwall.

3. Water derived from the non-calcareous Carboniferous rocks occurring in Derbyshire, Yorkshire, Lancashire, and North Staffordshire, which are only slightly pervious. Much of this water has not more than six degrees of hardness, but it is often highly charged with organic matter.

4. Water yielded by the calcareous Carboniferous rocks, such as mountain limestone and limestone slates. These occur in Northumberland, North Yorkshire, Lancashire, and Mid-Derbyshire. Since these rocks are less impervious, and are more easily weathered, they do not yield a very soft water—the hardness is sometimes very high.

5. Waters obtained from secondary rocks stretching from the mouth of the Tees to the mouth of the Exe, with a branch running to the mouth of the Mersey.

They include such rocks as Lias, New Red Sandstone, Conglomerate, and Magnesian Limestone The water obtained from these formations is of variable quality

Upland surface water, owing to its short contact with the earth, approaches most nearly natural or rain water in composition When collected from cultivated land its nature is very variable, depending upon the geological formation, and the amount and kind of organic matter present

The following tables (*Report of the Rivers Pollution Commission*) show the average composition of samples collected from different geological formations The results are expressed in parts per 100,000

NON CALCAREOUS STRATA

	Igneous Rocks.	Metamorphic, Cambrian, Silurian, and Devonian Rocks	Yoredale and Millstone Grits and Non calcareous Portions of Coal Measures.	Lower London Tertiaries and Bagshot Bed.
Total solids	5·15	5·12	8 75	13 14
Chlorine	1 13	0 92	1 05	2·60
Nitric nitrogen	0 002	0 006	0 010	0 020
Ammonia	0 001	0 062	0 003	0 012
Temporary hardness	0 10	0 30	0 40	0 9
Permanent hardness	2 00	2 50	4 30	5 6

WATER FROM CALCAREOUS STRATA.

These show, as might be expected, much larger amounts of dissolved mineral constituents.

	Silurian and Devonian Rocks.	Mountain Limestone	Calcareous Portion of Coal Measures.	Lias, New Red and Conglomerate Sandstone	Magnesium Limestone.	Oolites.
Total solids	13 71	17 07	22 79	18 92	17 84	17 46
Chlorine	1 20	1 24	1 52	1 50	1 40	1 55
Nitric nitrogen	0 021	0 011	0 016	0 012	0 00	0 042
Ammonia	0 00	0 001	0 003	0 002	0 001	0 604
Temporary hardness	1 2	5 7	4 0	7 8	6 4	6 6
Permanent hardness	7 4	7 0	8 3	6 3	8 3	5 8

WATER FROM CULTIVATED LAND

These show considerable differences, depending both upon the nature of the strata and cultivation

	Non Calcareous District	Calcareous District.	Average of Calcareous Districts.
Total solids	9 52	110 40	30 08
Chlorine	1·49	12 75	2 24
Nitric nitrogen	0 089	1 005	0 257
Ammonia	0 007	0 030	0 005
Temporary hardness	0 6	26 30	12 4
Permanent hardness	4·3	42 10	8 2

Subsoil Water.—Lying immediately beneath the surface soil is a stratum termed the "subsoil." This may be either pervious or impervious to water, according to its composition. If it be composed of sand, sandstone, chalk, gypsum, or other pervious substances, water will penetrate it readily. If an impervious stratum, such as clay, lies immediately below this subsoil, the water remains, and may be obtained from shallow wells bored into the subsoil. Such water is termed subsoil water. If the subsoil be impervious, the rain which falls upon the surface cannot penetrate it, and must either flow away over the surface or remain in the upper soil, forming a marsh or water-logged area. Thus the quantity of water which penetrates into the subsoil depends upon the slope of the ground and the nature of the subsoil. Large quantities of water are obtained from comparatively shallow wells sunk into the subsoil by extending them in all directions by means of horizontal galleries. The water supply of villages and country houses is largely drawn from the subsoil. The quality of the water is very variable. In the neighbourhood of dwellings it is often polluted with sewage and other organic matter, while if the subsoil contains soluble salts, such as gypsum or chalk, much of these will be dissolved and the water will be hard. Subsoil water may, therefore, be quite suitable or unsuitable for use in bleaching. Its variable nature is indicated by the following table:—

	Parts per 100,000.			
	1	2	3	4
Total solids . . .	25·50	148 00	58·80	228 00
Chlorine	3·44	7 81	5·68	25·00
Nitrogen as nitrate . .	0·30	2 10	0·44	3 55
Free ammonia . .	0·002	0·021	0·005	0 000
Albuminoid ammonia .	0 006	0·025	0·001	0·025
Temporary hardness .	12·45	29·00	25·00	35·00
Permanent hardness .	2·00	40·00	10·50	80·00

In Samples 2 and 4 the difference between the total hardness and total solids is due chiefly to the presence of sodium sulphate.

Deep Well Waters.—Deep wells are those which are bored through the subsoil, and impermeable stratum which lies beneath it, into the water-bearing strata below. The sides of such wells are made impervious to water, so that only that from the deep stratum is collected. Since the water may have travelled a long way through the earth to reach these water-bearing strata, it will have been subjected to a long process of natural filtration and purification. Hence deep well waters are, organically, among the purest known. They may, however, become polluted by subsoil water finding access through a fissure or fault in the overlying strata But, while organically pure, the dissolved mineral constituents may be considerable in quantity, particularly in the case of water from limestone formations. Hence they are not always suitable for bleaching. Examples are shown on p 194.

Samples 1 and 2 are good water, but No. 3 was found to be polluted by subsoil water entering through a fault in the rock. This water was being used for bleaching with unsatisfactory results.

	Parts per 100,000.		
	1	2	3
Total solids	12 00	25·00	92 00
Chlorine	1 42	2·50	9·10
Nitrogen as nitrate	0 02	0·00	1·05
Free ammonia	0·000	0·000	0·40
Albuminoid ammonia	0·010	0·005	0·020
Temporary hardness	8·50	18·50	25·00
Permanent hardness	1·50	2 50	50·50

These different kinds of water may be illustrated by the following diagram (fig. 68), in which the arrows indicate the course of flow and passage of the rain over the surface of and through the earth.

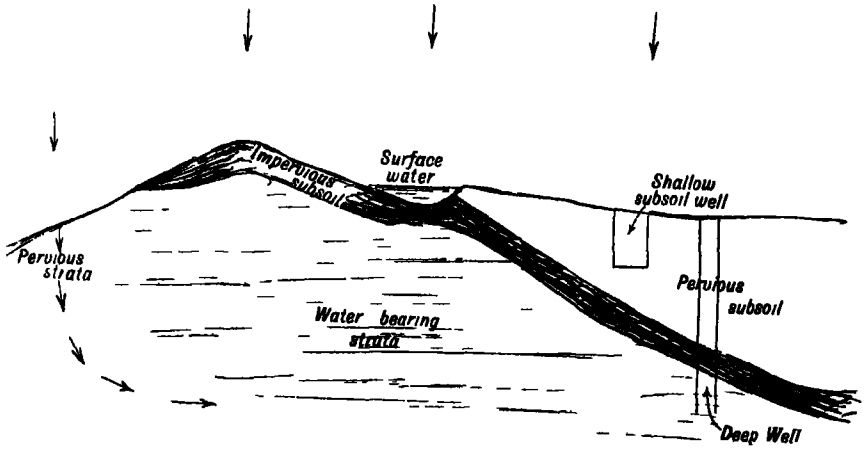


FIG 68.

The Impurities of Natural Waters, their Effects in Bleaching, and their Removal.

The different kinds of impurities met with in natural waters have been mentioned above. These must now be discussed more fully.

Suspended matter, from whatever source it is derived, is objectionable. Suspended organic matter is accompanied generally by micro-organisms. These may attack cellulose or the dressing materials used, producing tendering and discolorations, or decomposition of dressing. Mineral matter in suspension may contain iron oxide, which is the cause of both stains and over-bleaching. But suspended matter can be removed by an efficient filter.

Dissolved Gases.—All natural waters contain the gases of the atmosphere. In addition, carbon dioxide may be taken up during its passage through the earth. Mineral waters and those highly polluted with sewage sometimes contain sulphuretted hydrogen. Even traces of sulphuretted hydrogen would be sufficient to condemn a bleaching water, if this has not been done already upon

other grounds. Oxygen and carbon dioxide are the most important dissolved gases. Carbon dioxide is very readily soluble in water. At 0° C. and 760 mm. pressure water dissolves 1·75 times its volume of the gas. Oxygen is not so soluble At 0° C. and 760 mm pressure water dissolves about 7 c.c. per litre, or 1 part by weight per 100,000. Surface waters are commonly saturated with oxygen. Those obtained from deep wells contain less, but no natural water is free from it. Dissolved gases may be expelled from water by heating it. Thus, nearly 90 per cent. of the dissolved oxygen is driven off from water at 60° C. and the whole of it at 100° C. Dissolved carbon dioxide and oxygen may be removed also by chemical means. Thus, carbon dioxide may be precipitated as calcium carbonate by means of lime water, whilst oxygen can be removed by the addition to the water of a readily oxidised substance, such as ferrous hydroxide, which becomes changed into basic ferric oxide—

$$CaO+CO_2=CaCO_3$$
$$2Fe(OH)_2+O+H_2O=Fe_2(OH)_6.$$

Dissolved oxygen and carbon dioxide are of importance, because they tend to make water corrosive when used in boilers. This will be referred to again later.

Dissolved organic matter cannot be removed by filtration, though if water containing it be exposed to the air in thin layers it is oxidised gradually, giving nitrates in the case of nitrogenous constituents. But water which is polluted with organic matter is unsuitable for use in bleaching This is particularly the case if the organic matter be of animal origin, such as sewage. Sewage always contains putrefactive organisms, traces of iron, much saline and albuminoid ammonia, together with salts, such as sodium chloride. Moreover, animal proteins contain sulphur, which under the influence of certain bacteria is changed into sulphuretted hydrogen. Sewage, or similar pollution, is indicated by high values for chlorides, saline and albuminoid ammonia. Decomposing animal matter gives a considerable quantity of all of these. Vegetable matter gives more albuminoid than saline ammonia and comparatively little chloride. As a general rule it may be said that if a water contains more than 0·025 parts of either saline or albuminoid ammonia per 100,000 parts it is unsuitable for bleaching without careful investigation. Even an effluent from a sewage works should not contain more than 0·05 parts per 100,000.

Iron may, as already mentioned, be closely related to sewage contamination, but many unpolluted natural waters may contain it, sometimes in serious quantity. The presence of iron need not, as a rule, be considered if the water is to be softened, since it will be removed with the hardness. Ferruginous water may prevent the production of a fine white colour. This would be particularly likely in the case of goods containing unremoved tannic acid, with which iron forms a black-coloured compound. It should always be remembered that many of the chemicals which are used in bleaching works contain variable but distinct quantities of iron, which are more often the cause of discolorations than the water. It is difficult to say how much iron should be permitted. Much depends upon the method of treatment adopted, but if the goods are finished out of acid it is imperative that, after this point, no iron should be present. Goods for dyeing must also be quite free from iron.

Salts of Calcium and Magnesium.—From the point of view of the bleacher the compounds of calcium and magnesium (constituting hardness) are very objectionable. Hard water is a less powerful solvent than pure water. It reacts with some of the constituents of cotton or with reagents used in purifying

it, thus delaying or inhibiting chemical reactions. It causes, also, a great waste of soap and may give rise to stains and discolorations in finished goods.

Hardness in water is due to the presence of the following dissolved salts :—

1. Calcium bicarbonate, $Ca(HCO_3)_2$; magnesium bicarbonate, $Mg(HCO_3)_2$.
2. Calcium sulphate, $CaSO_4$; magnesium sulphate, $MgSO_4$, and other salts of these metals, such as chlorides.

Hardness due to bicarbonates of calcium and magnesium is termed "temporary," while that caused by other salts is known as "permanent," hardness.

Temporary Hardness.—Although pure water only dissolves calcium or magnesium carbonate to a slight extent, yet when it contains dissolved carbon dioxide the insoluble carbonates are converted into soluble bicarbonates, as shown by the equations

$$CaCO_3+CO_2+H_2O=Ca(HCO_3)_2,$$
$$MgCO_3+CO_2+H_2O=Mg(HCO_3)_2$$

Thus, the presence of temporary hardness in water is always due to carbon dioxide. These soluble bicarbonates are readily decomposed when heated, reforming the normal carbonates and giving off carbon dioxide When water containing temporary hardness is boiled, this change takes place, and the carbon dioxide being insoluble in boiling water is expelled. The carbon dioxide free water is no longer able to dissolve the normal carbonates These are therefore thrown down as a precipitate, the water at the same time becoming soft. This is shown in the equation

$$Ca(HCO_3)_2=CaCO_3+H_2O+CO_2$$

Thus, temporary hardness may be defined as that caused by bicarbonates of calcium and magnesium, and which is precipitated by boiling

Permanent Hardness.—This is due, chiefly, to the presence of sulphates and chlorides of calcium and magnesium These compounds are readily soluble in water, and their solubility does not depend upon the presence of dissolved carbon dioxide. Nor are they less, but, on the contrary, more soluble in hot than cold water. Boiling the water, therefore, does not affect the hardness due to these salts, and hence it is termed "permanent."

Expression of Hardness.—Hardness is generally expressed in terms of calcium carbonate, $CaCO_3$ This applies to both temporary and permanent hardness, and is irrespective of the nature of the salts, *i.e* bicarbonates, sulphates, chlorides of either calcium or magnesium are all stated as calcium carbonate. For certain purposes, such as water softening, it is necessary to distinguish between hardness caused by magnesium and calcium, but for ordinary use the common method of description is more convenient Hardness is expressed quantitatively in two ways, viz (1) degrees, and (2) parts per 100,000 There is some confusion in the use of these terms, but, as a rule, "degrees" refer to grains of calcium carbonate per gallon of water The term parts per 100,000 is better and explains itself. The two methods of expression are interchangeable. Thus, 5 degrees of hardness means 5 grains of calcium carbonate per gallon Since 1 gallon of water contains 70,000 grains and 1 lb. 7000, parts per 100,000 may be converted into grains per gallon or degrees by multiplying by 0·7, or *vice versa*, grains per gallon divided by 0·7 give parts per 100,000.

Hence, 5 degrees of hardness are equivalent to $\frac{5}{0{\cdot}7}$, *i e.* 7·1 parts per 100,000.

The Properties of Hard Water.—When pure soap is heated with alcohol it dissolves, forming a clear solution which, if diluted, remains liquid when cold. If a little of this solution be added to some distilled water placed in a stoppered bottle, the water remains clear, *i.e.* the soap is dissolved. If, now, the stopper be replaced and the bottle shaken, a foam or lather is produced. If hard water be placed in the bottle a different result is obtained At first, upon adding the soap solution, the water becomes turbid or opalescent As more soap is added a precipitate may be produced. If the bottle be shaken, no lather is formed, at any rate, till a much larger volume of soap solution has been added than was necessary for the distilled water. This is due to the fact that soluble salts of both calcium and magnesium decompose soap with the formation of insoluble calcium and magnesium soaps. Sodium oleate, $C_{17}H_{33}COONa$, is a typical soap. It reacts with soluble calcium and magnesium salts in the manner represented by the equations

$$2C_{17}H_{33}COONa + Ca(HCO_3)_2 = \underset{\text{calcium oleate}}{(C_{17}H_{33}COO)_2Ca} + 2NaHCO_3,$$

$$2C_{17}H_{33}COONa + MgSO_4 = \underset{\text{magnesium oleate}}{(C_{17}H_{33}COO)_2Mg} + Na_2SO_4.$$

If the addition of the soap solution be continued, the sodium soap is decomposed as long as any hardness remains in the water, and no lather is formed when the bottle is shaken. Only when all the calcium and magnesium salts have been decomposed will the addition of more soap solution produce a lather. In order to exercise its cleansing properties, soap must be in solution and must form a lather. Insoluble soaps are useless. Moreover, their presence interferes with the lathering power of a soluble soap.

For 1 gallon of distilled water about 10 grains of soap are required to form a permanent lather Each degree of hardness in the water makes the addition of a further 6 grains of pure soap necessary, while in the case of commercial soaps at least 10 grains are required to produce the same results. A water containing 35° of hardness will require 350 grains of soap per gallon or 1 lb. for 20 gallons. Hence the use of hard water would cause a great waste of soap

Calcium and magnesium soaps are sticky when wet If hard water be used in scouring cotton goods, these soaps adhere to the fabrics or may be precipitated within them These soaps are, as a rule, white when freshly prepared and dried, but they are decomposed gradually upon exposure to air, or when heated, becoming yellowish or brown in colour. This is more marked in the case of magnesium than of calcium soaps The development of colour depends upon the nature of the oil from which the soap was made, and those containing resin produce more colour than others. If the original soap was made from an oil with a distinctive odour, like cotton-seed oil, the gradual decomposition of the calcium and magnesium soaps produces a smell reminiscent of the oil. In the light of these remarks it is easy to understand what happens when cotton goods are washed with soap and hard water. The soap, instead of dissolving and being subsequently washed away by the water, is decomposed and deposited on the fabric as insoluble calcium or magnesium soap. The goods "appear" to be quite free from soap very quickly, but in reality they are not. When they are dried and kept, the insoluble soaps which they contain are liable to cause loss of colour or stains.

If hard water be used in the boiling of goods with caustic soda, it may prevent the complete removal of both proteins and oil by delaying hydrolysis and saponification. The authors, Trotman and Pentecost (*J.S C.I.*, 1905, p. 267),

boiled equal weights of cotton with a 2 per cent. solution of pure sodium hydroxide made (*a*) with distilled water, and (*b*) with water containing 40 parts of calcium sulphate per 100,000. After boiling for two hours, the solution was poured off and the residual cotton washed thoroughly with water, the washings being added to the sodium hydroxide solution. The soap and oil and also the proteins were then determined in each solution In every case it was found that when hard water was used less oil and nitrogen had been extracted than when distilled water was used. In different experiments from 10·9 to 19·7 per cent more oil and from 13·7 to 20·0 per cent. more protein was extracted by distilled than by the hard water.

Sodium chloride and sulphate are sometimes found in considerable quantities in natural waters. They tend to inhibit the hydrolysis of soap solutions and thus lower their detergent power. They retard, also, the saponification of fat by sodium hydroxide and the solution of the nitrogenous constituents of cotton. If these salts are present in large quantities they cause finished goods to have a damp feel. Thus, three pieces of the same cotton fabric were finished with distilled water and with water containing 17 grammes per gallon of sodium chloride and sulphate respectively. They were, after drying, exposed to the air for a few days, and the water content then determined The results were—

(1) 3·85 (2) 7·50. (3) 7·00

Nos. 2 and 3 felt distinctly damp by comparison with No 1. It is supposed that sodium sulphate and chloride also detract from the lathering power of soaps, but experiments made by the author do not confirm this view On the other hand, they do actively hinder pedesis (*q v*). Owing to their power of attracting water they frequently prevent goods from retaining a fine colour and dry appearance when finished, and this perhaps is an objection that can be urged against softening a very hard water, since the equivalent of the permanent hardness is always left in solution as sodium sulphate The following is an illustration of a water containing excess of both sodium sulphate and chloride —

	Parts per 100,000
Sodium chloride	12 87
Sodium sulphate	23 32
Magnesium carbonate	8 79
Calcium sulphate	8 75

When this water is softened the sodium sulphate will be still further increased by an amount equivalent to the calcium sulphate present, or 9 18 parts Thus the softened water will contain, per 100,000 parts—

Sodium chloride	12 87
Sodium sulphate	32 50

Sodium chloride and sulphate inhibit to a marked extent the hydrolysis and removal of the impurities of cotton by caustic soda This has been shown by experiments made by the author which will be referred to later

Scale-forming and Corrosive Waters.—Hard water cannot be used for steam-raising without considerable risk of causing damage to boiler plates, owing to the formation of scale Both hard water and water containing other dissolved impurities, such as salts of sodium or the gases of the atmosphere, may cause corrosion or pitting of boilers, or induce frothing or priming

Scale-forming Waters.—Scale is formed by hard water in two ways. When the water contains temporary hardness the bicarbonates become decomposed in the boiler and the liberated carbon dioxide escapes with the steam.

The calcium or magnesium carbonate, which is simultaneously formed, settles on the boiler plates, forming a scale. If no permanent hardness be present this deposit is comparatively easily detached, or it may even be granular and not attached to the plates. When water containing permanent hardness is continuously concentrated in a boiler, the sulphates of calcium or magnesium are deposited, together with the temporary hardness. Owing to the greater solubility of the sulphates they are deposited more slowly than the carbonates. For this reason the scale formed is much harder and is more difficult to remove from the plates, a chisel and hammer often being required.

Composition of Boiler Deposits.—Boiler deposits or incrustations generally consist of calcium and magnesium sulphate or carbonate, in proportions varying with the composition of the water, mixed with silica and iron oxide. The deposits containing much calcium sulphate are the most troublesome to deal with. The following are analysis of typical deposits :—

	Parts per 100.			
	1	2	3	4
Silica	13 18	0 47	.	1 07
Iron oxide	29 12	2 24	0 52	1 48
Lime	16 80	44 38	38 20	49 54
Magnesia	0·50	0 82	3·62	1·78
Sulphuric acid	18·47	28·22	48 41	5·82
Carbon dioxide . .	21 58	19·25	3 40	34·50
Organic and undetermined matter	0·35	4·62	5·85	5·81

In a clean boiler the temperature of the plates should be approximately that of the water. This has been shown by Stromeyer and Baron (*J I.M.E*, 1903, p. 773), who also found that a scale of $\frac{1}{8}$ inch in thickness raised the temperature of the plates by nearly 300° F. Rankine states that a scale of $\frac{1}{2}$ inch in thickness raised the temperature of boiler plates from 350° to 750° F. Thus, where *a scale is present the plate has to be heated to a very much higher temperature* in order to convert the water into steam. Further, every time the doors of the furnace are opened and cold air gains access, there is great contraction of the plates. This will be much greater than that of the adherent scale, and thus unequal stresses or strains are set up which gradually weaken and wear out the best plates. When the scale is thick there is also a considerable loss of heat owing to its non-conducting power

Rankine proved that carbonate and sulphate of calcium offer respectively seventeen and forty-eight times the resistance to the passage of heat that iron does, and from these figures calculates the following extra expenditure of fuel for the generation of steam as compared with a clean boiler :—

For a scale $\frac{1}{8}$ inch thick, 10 per cent.
" " $\frac{1}{4}$ " " 50 "
" " $\frac{1}{2}$ " " 150 "

Other observers, however, do not confirm these figures, but it is certain that a scale of any considerable thickness considerably increases the consumption of fuel.

Gardner and Lloyd (*J.S.C.I.*, 1905, p. 392) calculate that, assuming that 1 lb.

of coal at eight shillings per ton will convert 9 lbs. of water into steam, the cost of evaporating 1000 gallons of water would be four shillings, whereas the cost of the water, even including softening, should not exceed sixpence. It is probably correct to say that a water of 20° of hardness will cause a loss of 15 or 20 per cent. in fuel, which means an increase of about one shilling in the cost of evaporating 1000 gallons.

The deposition of scale is prevented to a certain extent by the use of alkaline solution of tannic acid and proprietary preparations. The luminator process is very simple and had, at one time, a considerable vogue. The water is allowed to run down plates of aluminium of special dimensions and having corrugations of a particular size, depending upon the water to be treated. Storage tanks and mains, if far from the boiler, must be coated with a non-conducting composition, such as bitumen, and the water must reach the boiler as soon as possible after treatment. The theory of the action is that the passage of the water over the aluminium plates induces a current of electricity, the water being negative and the metal positive electrodes. This current causes ionisation of the salts, which makes them fall in an amorphous form. At the same time aluminium goes into solution in a colloidal solution.

Corrosive Waters.—Many waters are found to corrode the plates or pipes of boilers, and the damage caused in this way may be more serious than that due to scale. Corrosive waters owe their properties to the following causes:—

1. The presence of salts which, like magnesium chloride, are hydrolysed when heated with steam.
2. Neutral salts of sodium, such as sodium chloride and sulphate.
3. Bicarbonates.
4. Dissolved oxygen and carbon dioxide.
5. Variations in composition of boiler plates.

Magnesium chloride is sometimes a contributory cause When a solution of this salt is evaporated it undergoes decomposition with the formation of a basic chloride and hydrochloric acid, in accordance with the equation

$$MgCl_2+H_2O=MgOHCl+HCl.$$

This decomposition is more marked at high temperatures, such as obtain in a boiler. Bailey and Johnston (*J S.C I.*, 1899, p. 456) state that the liberated hydrochloric acid may accumulate in the boiler till a concentration of 1 per cent. is reached, and that damage may be done to the boiler plates long before any hydrochloric acid can be detected in the distillate. If the acid be allowed to distil, it attacks the condensing pipes and carries iron or other metals over into the condensed water. Magnesium chloride attacks iron in contact with copper or another metal more readily than it does iron alone. This is, of course, due to the formation of an electric couple. Even slight differences in the composition of two adjacent plates is sufficient to bring about this result The addition of an alkali to the water, or the presence of calcium or magnesium carbonate, tends to inhibit the decomposition of magnesium chloride.

It is possible that corrosion by free acid may sometimes be due to another cause. Heinzelmann (*J S.C.I.*, 1914, p. 1079) has made the rather important observation that at a pressure of 10 atmospheres silicic acid, if present in water, liberates strong acids, such as sulphuric or nitric, from their sodium or other salts

The action of magnesium and other salts has been studied by Ost (*J.S.C I.*, 1902, p. 1177), who evaporated solutions of the chlorides and sulphates of the alkali metals in an iron boiler at 10 atmospheres pressure in the presence of

salts of calcium and magnesium. In all cases, even with distilled water alone, hydrogen was given off and magnetic oxide of iron found in the residue, but no iron was dissolved except in the presence of magnesium salts. The evolution of hydrogen is due to the decomposition of water by the iron, and the magnesium salts, instead of attacking the metal, react on the iron oxide in accordance with the equation

$$Fe(OH)_2+MgCl_2 \rightleftharpoons FeCl_2+Mg(OH)_2.$$

The action is reversible, but only partially. The addition of calcium carbonate diminishes the amount of iron dissolved by magnesium salts, an amount of calcium carbonate equivalent to about one-quarter of the magnesium salts entirely preventing the solution of the iron. At the same pressure, in the absence of air, a copper boiler was attacked by both magnesium and sodium chlorides, but the reaction seemed only to take place in the presence of cuprous oxide, from which it was almost impossible to free completely the boiler.

Other salts, particularly those of the alkali metals, have also some influence in causing corrosion. Sodium chloride and sulphate are commonly present in natural and always in softened water. Their corrosive action is probably due to the liberation of acid by electrolysis due to the formation of local electrolytic couples at the surface in contact with the solution and the atmosphere, or at points where inequalities in composition of metal exist.

Contact with a second metal, and overheating, generally increases liability to corrosion. Heyn and Bauer (*J.S.C.I.*, 1908, p 569) found that copper and nickel both increase the rate of rusting, but brass, manganese, and phosphorus have only a small effect. With few exceptions all salts behave similarly. In weak solutions rusting occurs more slowly than in water, the rate increasing with the concentration till a "critical" concentration is reached. The rate of attack of these critical solutions is usually higher than that of water, but is lower in the case of potassium, sodium, calcium and barium chlorides, sodium sulphate, and sodium and calcium bicarbonates The rusting in solutions of critical concentration is very irregular. The results of these experiments seemed to show that, contrary to common belief, alkaline chlorides and sulphates do not cause iron to rust more rapidly than water alone, and that alkaline carbonates are not always protective except at considerable concentrations Experiments carried out by the authors, on the other hand, appear to indicate that at the high temperatures of steam boilers, concentrated solutions of neutral salts do attack iron even when there is no possibility of an electrolytic couple being present.

Later work tends to prove that neutral salts do not cause corrosion in the complete absence of oxygen. It may start, but soon ceases or drops to a negligible quantity. Rust accelerates the action, but it may also reduce corrosion by adhering to the metal and forming a protective coating. Goudriaan (*J.S.C.I.*, 1919, 822A), dealing with corrosion by electrolysis, concludes that in air-free water electrolytic action is very small. In the presence of air the corrosive action of salts increases with concentration till the "critical" concentration is reached. Further concentration diminishes the corrosion, and a "limit" concentration is obtained which inhibits it entirely. The greatest corrosion is always where the iron is in contact with both air and water. The condition of the metal is an important factor. Impurities set up different potentials and induce secondary effects. Metals may be protected by covering with one of lower potential, while contact with one of higher potential, such as nickel or copper in the case of iron, increases the rate of corrosion. The critical concentration tends to fall with rise of temperature.

But others, as mentioned above, incline to the view that oxygen is not essential to the setting up of corrosion by electrolysis. M'Lellan (*J.S.C.I.*, 1917, p. 853) gives the following example of this. The water contained per 100,000 parts and was free from oxygen

Total alkalinity	212 6	Total hardness .	35 5
Chlorides	305 7	Lime hardness .	23 3
Sulphates . . .	1390 3	Magnesia hardness	12 2
		Alkalis	2233 1
Total acids .	1908 6	Total bases	2268·6

He is of opinion that the cause of corrosion may be solely electrolysis.

He discusses, also, certain other conditions which have been observed to accelerate or retard corrosion. While small quantities of caustic soda have little effect on corrosion, sodium carbonate stimulates it. M'Lellan suggests that if excess of sodium carbonate be present it may liberate carbon dioxide by decomposition in the boiler. This would attack the plates, forming ferrous carbonate Thus there would be two electrodes, viz. iron and ferrous carbonate, which would probably set up a difference of potential and cause corrosion. Sodium hydroxide inhibits the liberation of carbon dioxide by dissociation. Or the carbon dioxide may act in the manner shown in the equations if oxygen be also present.

$$(1)\ Fe+H_2O+CO_2 = FeCO_3+H_2.$$
$$(2)\ 4FeCO_3+O_2+6H_2O=2Fe_2(OH)_6+4CO_2$$

At boiler temperatures equation (2) might be

$$3FeCO_3+O=Fe_3O_4+3CO_2$$

Bicarbonates.—These when heated give rise to carbonic acid, which attacks iron with the formation of ferrous carbonate.

Dissolved Oxygen and Carbon Dioxide.— These are undoubtedly the chief agents causing corrosion Carbon dioxide, when present alone, acts as stated above like any other acid, forming ferrous carbonate and hydrogen The action of dissolved atmospheric carbon dioxide would be very small compared with that of carbon dioxide liberated in the boiler by the decomposition of bicarbonates

Tillmans and Heublein (*J S.C.I*, 1917, p 938) state that while carbon dioxide is not essential to corrosion, it accelerates oxidation when present There exists, however, a point of equilibrium between bicarbonates and free carbon dioxide—that is, for a definite amount of bicarbonate, a certain quantity of free carbon dioxide may be present in the water without causing corrosion. If this proportion of carbon dioxide be exceeded corrosion takes place. When a water containing calcium carbonate and free carbon dioxide, in amounts not exceeding those necessary for this state of equilibrium, acts on iron, the metal may be attacked first, but owing to the removal of carbon dioxide and deposition of calcium carbonate the action soon ceases If a large proportion of carbon dioxide be present the protective coat of calcium carbonate is not formed. But further, *in the complete absence of oxygen* no corrosion can take place.

If oxygen be also present, even small quantities of carbon dioxide become important. First, ferrous carbonate is formed. This is then oxidised by the dissolved oxygen to ferric carbonate, which, in turn, suffers decomposition with the liberation of carbon dioxide and the precipitation of iron oxide. This cycle

then recommences and may continue indefinitely as long as dissolved oxygen is present.

(1) $Fe+H_2CO_3 = FeCO_3+H_2$.
(2) $2FeCO_3+H_2CO_3+O = Fe_2(CO_3)_3+H_2O$.
(3) $Fe_2(CO_3)_3 = Fe_2O_3+3CO_2$.

Variation in the Composition of Boiler Plates.—According to Desch (*J.S.C.I.*, 1916, p. 51), local couples are caused chiefly by want of homogenity in the boiler plates. This may be due to either chemical or physical differences. Chemically pure metals may corrode by reason of local physical differences induced by mechanical means, such as cold working, by which films of amorphous material are formed between the separate crystal grains.

Evans (*J S.C.I.*, 1924, p. 222) has shown that it is possible to produce an electric current from a cell consisting of two strips of the same metal immersed in the same solution, one strip being aerated by bubbling air over it, whilst the

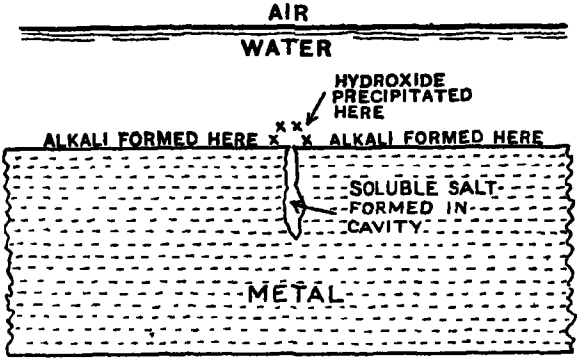


FIG. 69.

other is protected from access of oxygen. The current is provided by the corrosion of the unaerated metal and, if the resistance of the whole circuit be small, the unaerated strip actually suffers more corrosion than the aerated strip. Differential aeration may account also for the special corrosion set up in cavities. If a small cavity (fig. 69) exists in the surface of the metal into which oxygen cannot diffuse quickly, a current will be produced between the unaerated area within the cavity, which will become anodic, and the aerated part of the surface outside, which will be cathodic, but will not interfere with further anodic attack. At the mouth of the cavity, where the soluble metallic salt from the interior mixes with the alkali from the cathodic part outside, hydroxide may be precipitated, but it will not inhibit the anodic attack proceeding within. The rate of attack is determined by the supply of oxygen to the whole surface outside the pit, and since it is all concentrated on the small area within the pit, the rate at which the corrosion bores into the metal will be very great. This theory, it should be noted, explains also why rust of a loose flocculent character tends to promote further corrosion of the underlying metal, and accounts for the fact that corrosion appears to be specially rapid at just the points which are the least accessible to oxygen.

It appears from these experiments that the all-important thing for boiler feed waters is that they should contain no dissolved oxygen or carbon dioxide.

Water, at ordinary temperature and pressure, will dissolve about 1 part of oxygen by weight per 100,000 parts of water. All natural waters contain dissolved oxygen. Surface and subsoil waters are often fully saturated, those from deep wells contain less, but generally at least 0·2 parts per 100,000. No water-softening process removes oxygen; in fact, owing to agitation or mixing, the oxygen is liable to be increased by softening. While making the water more suitable for bleaching and dyeing we may therefore, at the same time, make it more corrosive by (1) increasing the amount of dissolved oxygen, (2) leaving bicarbonates in it, (3) adding sodium salts Modern practice, then, in treating feed waters is largely directed to removing dissolved oxygen.

The Removal of Dissolved Oxygen.—There are many ways in which oxygen can be removed from water. The following may be noted —

1. The whole of the oxygen can be expelled by heating the feed water to 100° C, and about 90 per cent of it is given up at a temperature of 60° C.

2 Both oxygen and carbon dioxide can be completely removed by treating the water with ferrous sulphate and sodium hydroxide. The ferrous hydroxide first formed absorbs oxygen rapidly, while carbon dioxide combines with the sodium hydroxide. If lime water is used, insoluble calcium carbonate is formed. The reactions are—

$$(1)\ FeSO_4+2NaOH = Fe(OH)_2+Na_2SO_4.$$
$$(2)\ 2Fe(OH)_2+O+H_2O=Fe_2(OH)_6.$$

3. The feed water is brought into contact with thin sheets of iron in a "de-activating tank" The corrosive action is thus exerted on a cheap, easily replaced metal instead of on the boiler plates

4. The water is sprayed over baffles in a de-activator, and free and dissolved gases removed by heat, vacuum, or by a combination of both.

5. A counter electromotive force may be employed, but according to Jones (*J.S C I*, 1914, p 1080) this is only effective when the amount of dissolved alkali chloride is equivalent to the calcium sulphate present

In the Cumberland process a counter electromotive force higher than that causing corrosion is introduced The shell of the boiler forms the cathode, the anode consisting of pieces of iron inserted in the water and insulated from the shell A continuous current is supplied by a dynamo, similar to that used for electroplating, working at 10 volts The process is said to be effective both for preventing corrosion and for preventing the formation of and the recovery of hard scale.

In another process (Eng. Pat 25893, 1913) graphite plugs are inserted into the carbon plates of compound zinc carbon elements which are in metallic connection with the boiler shell below the water line The passing of a suitable current causes the deposit of graphite on the boiler plates that come in contact with the heated water and thus protects them from corrosion.

Foaming Waters.—Waters containing organic or suspended matter often foam or prime naturally, but the most common cause is the presence of alkali or the salts of the alkali metals in too high concentration. M'Gill (*J S C.I.*, 1904, p 351) proved that all sodium salts produce foaming when present to a greater extent than 1 gramme per litre without pressure. When the water is heated under pressure the quantity necessary to cause foaming is much less According to M'Gill, 300 parts per million of any sodium salt, reckoned as Na_2O, render a water unfit for steam-raising. Priming is particularly undesirable when the condensed steam is to be used It is often caused by the injudicious addition of soda to a boiler or the continual use of boiler fluids of unknown or uncertain

composition. The following is an example of a water taken from a boiler which primed badly and showed high concentration :—

	Parts per 100,000
Sodium chloride	1050 00
Lime . .	108 68
Magnesia . . .	10 66
Sulphuric acid . . .	109 50

Foaming is frequently responsible for contamination of condensed water with iron. The question is indirectly connected with the use of softened water where the original hardness is high. As will be explained later, when hard water is softened there is, as a rule, an exactly equivalent amount of a soluble sodium salt left in solution. When such a water is used continuously for a boiler the concentration may become very great That this is so is seen in the following examples of boiler waters :—

	Parts per 100,000.	
Sodium sulphate	2162 00	1841 00
Sodium chloride . .	807 34	489 80
Sodium carbonate	114 48	93 29
Sodium hydroxide	193 60	156 80

CHAPTER XII.

WATER SOFTENING: INDUSTRIAL ANALYSIS OF WATER.

Water Softening.—All industrial waters having more than 6 parts of hardness per 100,000 will repay softening, while, where the hardness exceeds 10 parts, softening becomes a necessity if no better supply be obtainable.

The removal of hardness depends upon fixed chemical principles, combined with mechanical appliances for the measuring and mixing of the reagents and the separation of the precipitates produced.

Removal of Temporary Hardness.—Calcium and magnesium bicarbonates are removed by expelling or fixing the carbonic acid which holds them in solution. Thus, if the water be boiled, either directly or by means of live or waste steam, it quickly becomes turbid owing to the separation of calcium carbonate, and ultimately all the "lime" is precipitated—

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O.$$

Magnesium bicarbonate, owing to its somewhat greater stability, is not so readily thrown down as the calcium compound This reaction takes place in boilers, but is not readily available for outside softening, although elevation of temperature is always greatly to be desired in removing both temporary and permanent hardness.

The carbonic acid may be removed chemically by the addition of an alkaline hydroxide capable of combining with it, lime or caustic soda being most generally employed. Barium hydroxide may, however, sometimes be substituted with advantage. The alkali withdraws carbonic acid from the bicarbonates, forming alkaline carbonates, and as soon as the carbonic acid is thus fixed the temporary hardness disappears—

$$Ca(HCO_3)_2 + CaO = CaCO_3 + CaCO_3 + H_2O,$$
$$Ca(HCO_3)_2 + 2NaOH = CaCO_3 + Na_2CO_3 + H_2O$$

It will be observed that when sodium hydroxide is used, an equivalent of sodium carbonate is left in solution, which may be subsequently made use of for the removal of permanent hardness.

The removal of magnesium bicarbonate is not quite so simple as that of calcium. When lime or soda is added to water containing magnesium carbonate in solution, the carbonic acid is withdrawn as before, and calcium and magnesium carbonates are produced—

$$Mg(HCO_3)_2 + CaO = CaCO_3 + MgCO_3 + H_2O.$$

In order, however, to precipitate the magnesium carbonate, a second molecule of the precipitant is required, which converts it into hydrate, in accordance with the equations

$$MgCO_3 + Ca(OH)_2 = Mg(OH)_2 + CaCO_3,$$
$$MgCO_3 + 2NaOH = Mg(OH)_2 + Na_2CO_3.$$

Thus each molecule of magnesium bicarbonate present requires two equivalents of lime or soda for complete precipitation. In dealing with temporary hardness it is very important to remember that most natural waters contain some free carbonic acid, and that until this is neutralised it protects the bicarbonates. Therefore, in calculating the quantity of lime or soda necessary, not only the temporary hardness, but also the amount of free carbonic acid must be known. We have in water three distinct conditions in which carbonic acid exists, viz —

1. Free carbonic acid.
2. Loosely bound carbonic acid, as bicarbonate.
3. Fixed carbonic acid, as normal carbonate.

If the free carbonic acid is not determined and allowed for and the allowance occasionally verified, incomplete softening may result

Removal of Permanent Hardness —Calcium sulphate is generally precipitated by means of sodium carbonate, double decomposition taking place, resulting in the formation of insoluble calcium carbonate and soluble sodium sulphate—

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4.$$

Magnesium sulphate, again, is thrown down in two stages requiring two molecules of precipitant, one as carbonate and one as hydrate—

$$MgSO_4+Na_2CO_3=MgCO_3+Na_2SO_4,$$
$$MgCO_3+Ca(OH)_2=Mg(OH)_2+CaCO_3.$$

Magnesium sulphate may be also thrown down completely by caustic alkali as hydrate, $Mg(OH)_2$.

The reaction between bicarbonates and lime or soda may be carried out at ordinary temperatures, but the precipitation of permanent hardness is never quite completed without the aid of heat; that is to say, sodium carbonate and calcium or magnesium sulphate can both exist at ordinary temperatures in the same solution. Thus the removal of temporary hardness is a much simpler matter than the softening of permanently hard water; when this only has to be considered it is only necessary to mix the calculated quantity of lime with the water, allow the precipitate to settle, and draw off the supernatant soft water. In many cases this process is both satisfactory and cheap

Automatic Softeners.—Mechanical water softeners are very numerous, but all depend upon the above chemical reactions, the differences being chiefly in methods of manipulation.

The earliest form of water softener was *Clarke's*, in which sufficient lime was added to remove the temporary hardness, the precipitate being allowed to settle, the permanent hardness being neglected. The method is still quite satisfactory for waters containing very little permanent hardness; but it was soon found that, in general, permanent hardness is more troublesome than temporary, although usually less in amount. Further, where a continuous supply of softened water is required, the time taken for the precipitate to settle becomes an objection and necessitates duplication of tanks. The use of a precipitant, such as aluminoferric, is some improvement, but still insufficient for modern requirements. These defects have led to the invention of many forms of automatic apparatus, in which the reagents are mechanically measured and mixed with the water, and the precipitate removed by means of filters, the rate of reaction being in many cases increased by the use of live or waste steam. Water softeners may be roughly classified as follows :—

1. Those working at ordinary temperatures.
2. Those working at elevated temperatures.
3. Those employing filters for the removal of the sediment
4. Those relying on gravity for the removal of the sediment.

In most cases more than one of these cardinal features is involved.
The essential parts of a water-softening apparatus are—

1. A reagent tank.
2. A reaction tank.
3 A precipitating tank with, or without, a filter.
4. A soft-water tank

With reference to those softeners working at elevated temperatures, it must be noted that they are rarely satisfactory where heat alone is relied upon to remove temporary hardness, since this can only be effected by somewhat prolonged boiling. This cannot be carried out by waste steam, and live steam is too expensive. Further, there is considerable danger of introducing oil and other objectionable matter with waste steam. Steam may be regarded as an assistant, but not as a satisfactory reagent. The reagent tank is usually connected with some mechanical apparatus for measuring and introducing the chemicals In some cases they are measured and introduced in bulk into a tank full of water subsequently mixed by a current of air or by some similar device. This method, however, is not suitable where a continuous supply of softened water is required ; hence it has generally been superseded by some continuous method of introducing the chemicals into the water as it flows into the reaction tank, thereby also reducing the cost and size of the apparatus. The reaction chamber must be sufficiently large to allow the chemicals time to complete their reactions. It should be approximately equal to the hourly duty of the plant (Royle, *J.S.C.I*, 1906, p 453). Where the reaction is also the precipitating chamber a somewhat larger capacity is desirable if danger of clogging the filters is to be eliminated

Filtration of the softened water is essential to a continuous apparatus, since the time required for the settling of the precipitate is rather long and variable In non-continuous processes, such as the Archbutt and Deeley, the filter is dispensed with, the old sludge being used to carry down the fresh precipitate The precipitating chamber is sometimes provided with shelves or partitions to arrest the precipitate, but, as a general rule, these are not sufficient. A great many materials are employed as filtering media, such as wood fibre, paper pulp, wool, gravel, and sand, the filtration sometimes being upwards, as in the case of the Paterson softener, and sometimes downwards, as with the Babcock-Willcox process The clogging of filters sometimes causes considerable trouble, and, according to Royle, gravel and sand are the only ones which give good results. Where sufficient space is available, it is very desirable to provide, even with a continuous softener, a settling tank and to draw the clear water from this tank through a filter The principles of water softening may be illustrated by the following apparatus (fig. 70).

A is a small cistern containing a mixture of sodium hydroxide and carbonate. It flows through a funnel into the corked reaction chamber B, entering at the bottom, and at the same time becoming mixed with the hard water entering from the main supply. The concentration of the chemicals and the rate of flow is such that in a given time approximately sufficient of the reagents are delivered to soften the water entering the reaction chamber during the same time. Through a second tube, E, reaching to the bottom of the flask, steam is passed to assist complete mixing and chemical reaction. A third tube, commencing just beneath

the cork, leaves the flask B and passes to the bottom of a second corked flask, C, which is the precipitating chamber. A second delivery tube leaves this chamber at the top, ending above a filter leading to the store tank D.

Limits of Softening.—Owing to the solubility of calcium and magnesium carbonates and magnesium hydroxide it is not possible to completely soften a hard water. From two to three degrees of residual hardness constitute a satisfactory result. Moreover, it is not always desirable to attempt to soften completely with sodium hydrate and carbonate, as in certain cases this cannot be done without leaving excess of sodium carbonate in the softened water. This will always be the case when the sum of the temporary hardness and that due to magnesia is greater than the permanent hardness. Archbutt (*J.S.C.I.*, 1891, p. 516) has shown that in the presence of excess of calcium hydroxide magnesium hydroxide tends to become colloidal and retained in solution. It is therefore

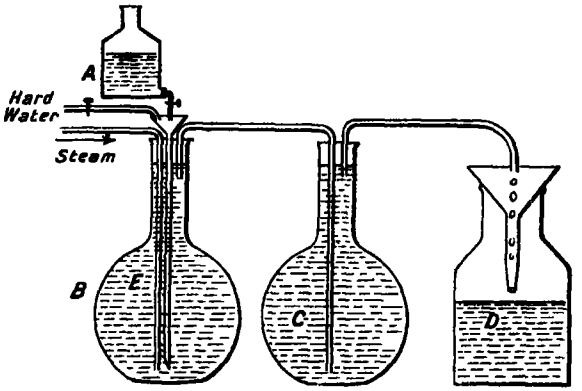


FIG. 70.

better not to add enough calcium hydroxide to precipitate completely all the magnesia present, but to stop just short of that amount. In this case the precipitate is granular and separates readily.

Calculation of Quantities of Reagents.—The quantities necessary may be calculated from the equations

(1) $Ca(HCO_3)_2+Ca(OH)_2 = 2CaCO_3+2H_2O$.
(2) $Mg(HCO_3)_2+2Ca(OH)_2 = 2CaCO_3+Mg(OH)_2+2H_2O$.
(3) $CaSO_4+Na_2CO_3 = Na_2SO_4+CaCO_3$.
(4) $MgSO_4+Ca(OH)_2+Na_2CO_3 = CaCO_3+Mg(OH)_2+Na_2SO_4$.

The reactions for chlorides and nitrates of calcium and magnesium are similar to those of the sulphates. The quantities of reagent cannot be calculated directly from the hardness unless the magnesia is also known. If, however, the temporary and permanent hardness are known and the magnesia is determined and calculated into its equivalent of calcic carbonate, Pfeifer's formulæ may be applied (Procter, *J.S.C.I.*, 1904, p. 10). They are as follows, the results being in lbs. per 100,000 gallons:—

Let Ht = Temporary hardness,
Hp = Permanent hardness,
Hm = Hardness due to magnesia,
then 5·6 (Ht+Hm) = lime required,
10·6 (Hp) = dry sodium carbonate required.

For the removal of temporary hardness alone by means of lime the quantity necessary is—

(*a*) 5·6 (Ht+Hm−Hp) where Hm is greater than Hp.
(*b*) 5·6 (Ht+Hm) where Hm is not greater than Hp.

For sodium hydrate and sodium carbonate the formulæ are—

(1) 8 (Ht+Hm)=caustic soda required.
(2) 10·6 (Hp−(Ht+Hm))=sodium carbonate required.

These formulæ show that when the sum of Ht and Hm is greater than Hp, free sodium carbonate will be left in solution.

These results, based upon volumetric hardness determinations, have not the same degree of accuracy as those resting upon gravimetric analysis Results based upon the soap tests are quite unreliable, and are sometimes the cause of apparently unsatisfactory results.

Gardner and Lloyd (*J.S.C.I.*, 1905, p 392) found that the usual methods of calculation cannot be relied upon to give accurate results in the presence of large amounts of neutral salts, such as sodium sulphate and chloride, since the equation

$$CaSO_4+Na_2CO_3=CaCO_3+Na_2SO_4$$

is, to a certain extent, reversible.

Selection of a Water Softener.—The type of softener selected must depend very much upon the available space, quantity, and nature of supply required and the source of the original water Thus, where water can only be obtained or is only required intermittently, a softener of the Archbutt-Deeley type is suitable, but where a constant supply is necessary some other form may be more desirable. Again, where much steam is available, a softener which works at elevated temperatures is indicated The number of water softeners is very great, and it would be impossible to describe them all. The following are selected as typical, but not necessarily the best.

Lassen and Hjort Water Softener.—This is a very good type of continuous water softener, as distinguished from non-continuous water softeners, such as the Archbutt-Deeley type. There are three essential features the reaction chamber, the settling chamber, and the filter. In a non-continuous water softener the filter is dispensed with, the precipitate being merely allowed to settle before the soft water is drawn off. In this process (fig 71), however, a constant stream of hard water is led into a reaction chamber, where it comes in contact with the chemicals, the mixture being heated by live or waste steam in order to make the softening more complete, it being possible to soften a water more completely when the temperature is raised than when heating is dispensed with From the reaction chamber the water passes into the settling chamber, and thence up through a suitable filter, and finally into a storage tank. The lime in this process is used in the form of milk of lime, which is about 100 times as strong as lime water, thus making it possible to reduce the size of the chemical tank.

Description of Apparatus.—The hard water passes along the pipe K into one of the chambers of the oscillating receiver R. When this chamber is filled, the centre of gravity is altered, causing it to tip up and pour its contents into the tank B, at the same time bringing the other chamber of the receiver under the orifice of the pipe K. To the side of the oscillating receiver is fitted a tank D containing the chemicals, lime and soda ash, or caustic soda. A valve is fitted to the bottom of D, actuated by a system of levers fitted to the oscillating receiver,

so that at each oscillation a given quantity of the chemicals can be mixed with the water. The water in the chamber B is heated to about 150° F. by means of live or exhaust steam. From B the water passes into the settling tank A, and from this upwards through filters of wood-wool packed tightly between rows of wooden bars. After softening and filtering the water flows into a storage tank O. The storage tank is fitted with a pressure float F, which regulates the flow of water in the pipe K, according to the height of water in the tank O.

Paterson Water Softener.—This apparatus (fig 72) is similar to the Lassen and Hjort softener, but differs in certain important respects It has

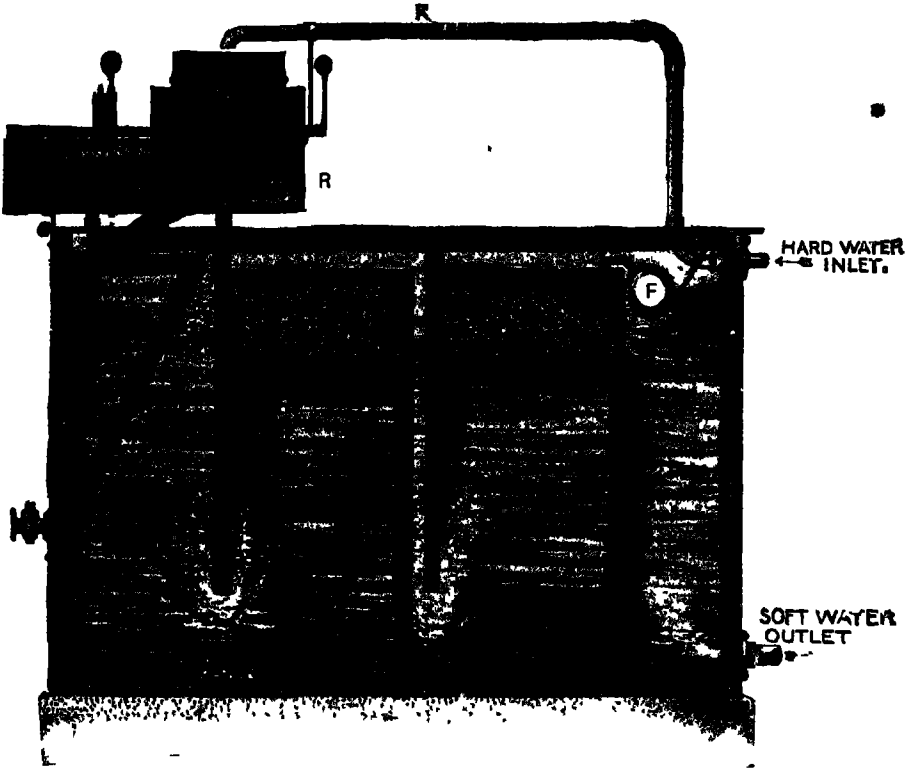


FIG. 71.—Lassen and Hjort's water softener

a mixing-box precipitating chamber and wood-fibre filter. The chemicals used are lime and soda, the lime being added to the hard water in the form of a saturated solution, instead of adding milk of lime, as is usual. The advantages claimed for this saturated solution are that, the strength of the solution being known, the exact calculated amount of lime can be added, whereas the strength of milk of lime varies with the quality of the quicklime used · lime water shows no tendency to choke the valve, and any inaccuracy in the amount added is inappreciable, as the solution is very dilute. In this form of softener a measuring gear is provided to register the flow of hard water before it comes in contact with the chemicals, and a float riding on the surface of the water regulates two valves, one controlling the discharge of soda, and the other the discharge of lime water. After passing through the wood-fibre filter, the water is led through

a filter bed of fine quartz sand, and finally through gun-metal strainers, fitted with phospho-bronze screens The quartz filter can be easily cleansed by reversing the current of water and injecting compressed air, and the screens are removable.

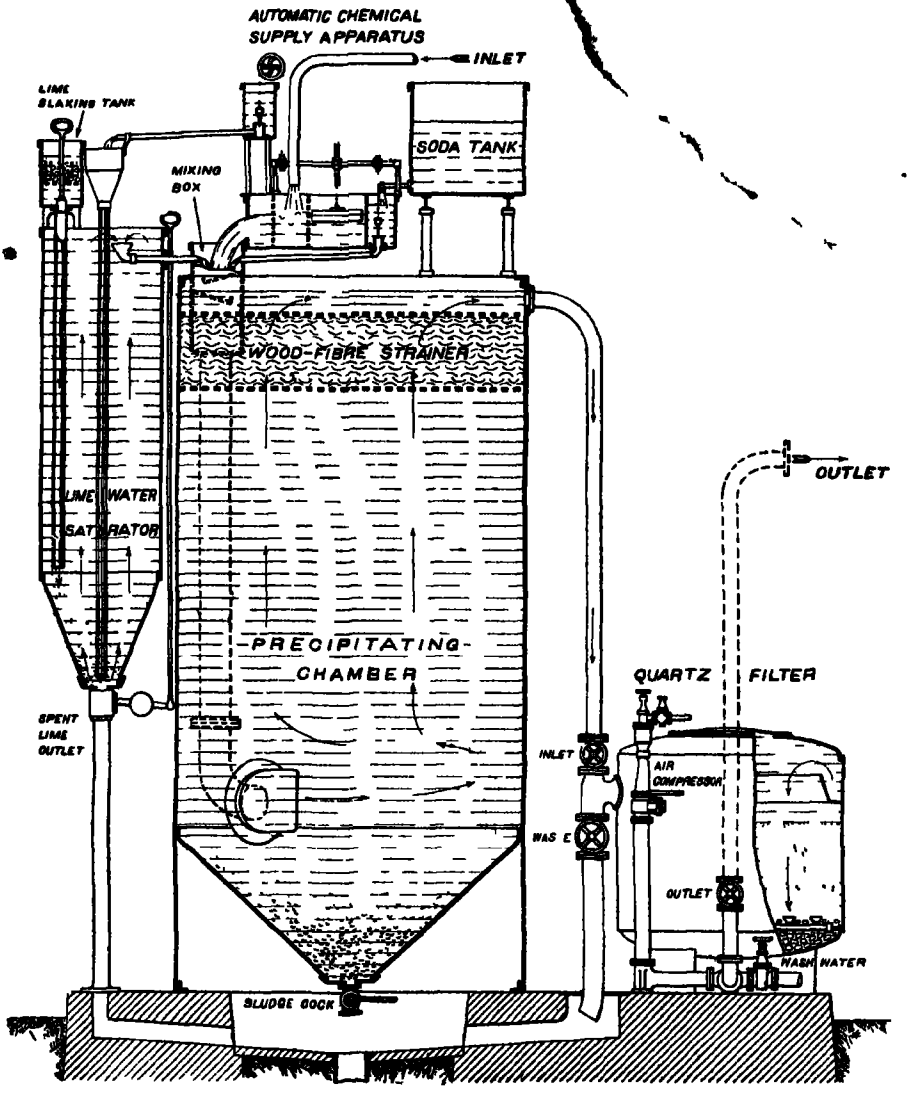


FIG 72.—Paterson's cold-process water softener

Process of Softening.—The day's supply of soda is dissolved in water and poured into the storage tank; a ball valve fitted to this tank maintains a uniform head of soda, to supplement that discharged through the outlet valves. Once a day the supply of milk of lime is prepared in the slaking tank and run into the saturator. A regulated supply of water passes down the central pipe to the

conical bottom of the saturator, and becomes saturated with lime on its way upwards. The lime particles settle out, and only a clear solution flows into the mixing-box, where it meets the hard water and soda. The mixture next passes through a mixing trough to the precipitating chamber; the bulk of the dissolved impurities are deposited here, while the water passes upwards and is filtered through wood-fibre. Where the highest purity is desired, the water is further freed from any trace of suspended impurities by filtration through the quartz filter, and finally run into the storage tank through the gun-metal strainers.

The Archbutt-Deeley Softener.—This softener (figs. 73–75) can be advantageously used when a continuous supply of soft water is not necessary. For a supply of water less than 6000 gallons per hour, one softening tank is sufficient if a storage tank is provided, but if a greater supply is required, two or more tanks must be used.

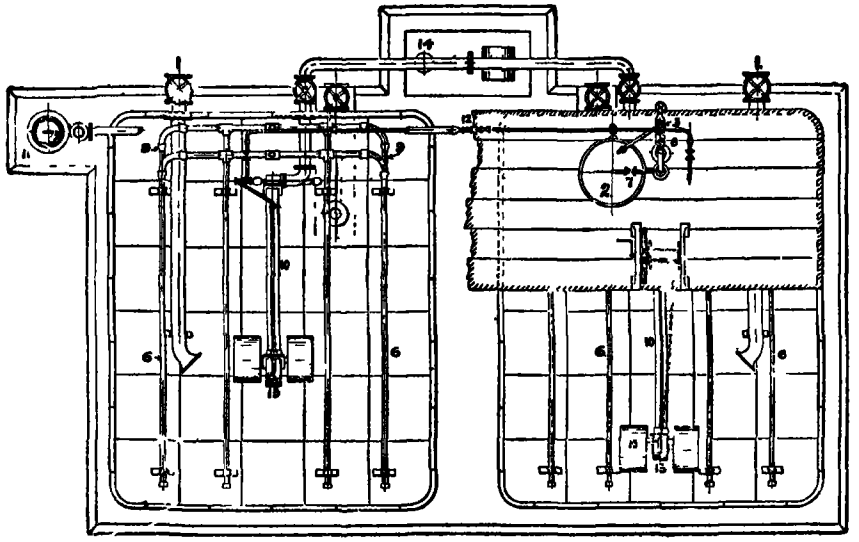


FIG. 73.—Plan

The apparatus consists essentially of a tank into which the water to be softened is run. A mixture of milk of lime and carbonate of soda is made in a small separate tank and run into the softening tank, the contents being thoroughly mixed. By stirring the sediment formed at the bottom of the tank in previous operations, this coarser precipitate carries down the more finely divided new precipitate and greatly hastens the settling. Better results are obtained with water containing magnesium salts, the hydrate of magnesia forming a coarse precipitate, which settles more quickly than calcium carbonate. After a water has been softened there is always a tendency for a small amount of residual hardness, not removed in the softener, to be deposited, and this is very liable to clog the feed pipes of the boilers. A special feature in the Archbutt-Deeley process is the removal of this tendency by carbonating the softened water, the sparingly soluble carbonates of lime and magnesia being converted into soluble bicarbonates.

Process of Softening.—The hard water is run into the tank by means of the supply pipe (1, fig. 73) up to the level of a gauge mark on the side of the tank

Whilst the tank is being filled the calculated quantities of quicklime and carbonate of soda are weighed out into the small tank (2, fig. 74) and boiled with water by means of live steam. In the case of certain waters it is necessary to add a little alumino-ferric This is added in the requisite proportion in the form of a standard solution, immediately after running in the chemicals. When the tank is filled to the mark, the inlet valve is closed, and steam is admitted to the blower (3), causing a current of water to circulate up through the rose (4), the three-way tap (5), down the vertical tube, and into the tank through perforations in a row of horizontal pipes (6). The three-way tap is then opened and the solutions of chemicals run into the tank and thoroughly mixed by means of the currents caused by the steam. (The parts of the apparatus numbered 3–7 will be best seen by reference to fig. 75.) Air is next blown through the perforations

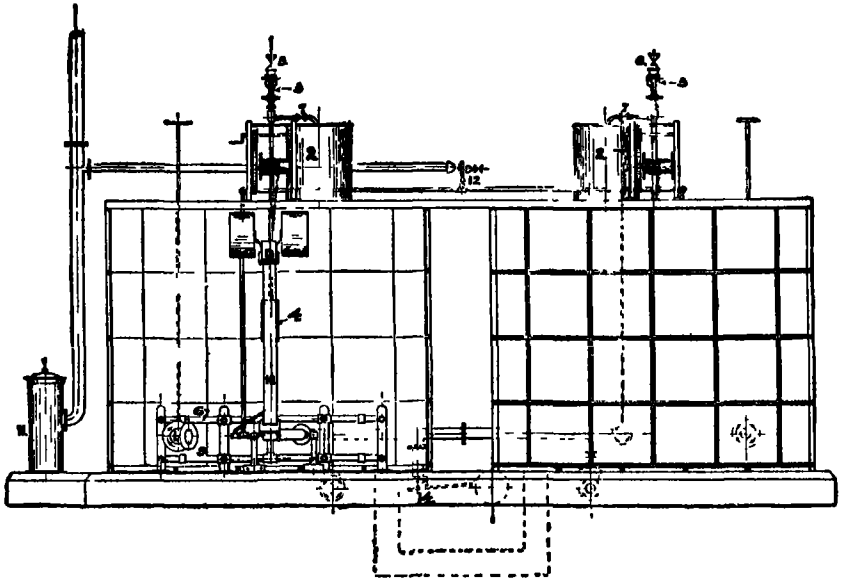


Fig 74.—Elevation, part in section, Archbutt-Deeley water softener (*Mather & Platt*)

in the pipe (6) by opening the tap (8), and then, by reversing the three-way tap (5), air is blown through the perforations in the under side of the lower tube (9), storing up part of the old precipitate in the tank. After air has been blown in for about ten minutes the precipitate is allowed to settle, and, after standing for about an hour, the water in the tank is practically clear to a depth of 6 feet from the surface The water is now allowed to run off through the mouth (13) of a hinged pipe (10), the mouth being kept just below the surface of the water by means of floats As the water flows down this pipe it is met by an ascending stream of carbon dioxide and air produced by burning coke, which is forced up the pipe, and this carbonates the softened water, which is now run into a supply tank.

The precipitate which collects at the bottom of the settling tank, technically known as "mud," must be removed from time to time. This is effected by means of a discharge pipe fitted with a plug, or in large tanks, and the mud is swept out through doors.

Harris Anderson Water Softener (Baron and Stromeyer, *loc. cit.*)—The apparatus (fig. 76) consists of a distributor, a lime tank, soda tank, air vessel and reaction tank, and settling tank with a filter. The distributor has a circular weir, the water flowing from the circumference to three central compartments, and thence to the air vessel, to the lime tank, and to the soda tank respectively. The air vessel, by means of its syphon, acts as an air pump and agitates the milk of

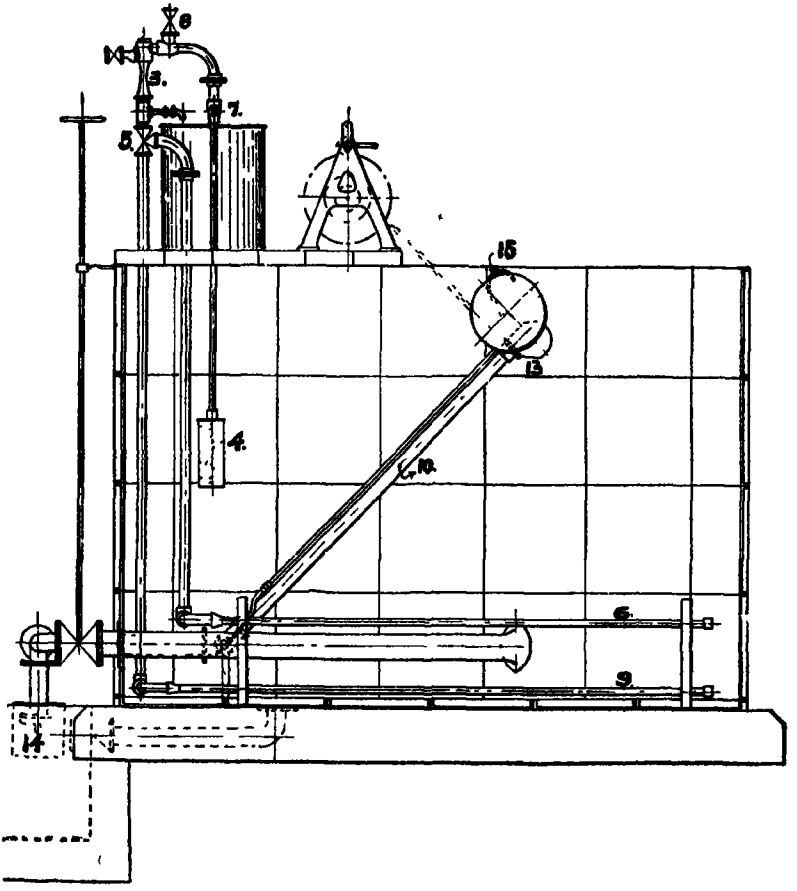


FIG 75.—Cross-section Archbutt-Deeley water softener.

lime in the lime tank, in which pipes and cones are arranged for this purpose. The soda tank consists of four cylinders, the solid soda being poured into a cage, the centre one, while the water flows into the second inner cylinder, and, according to the strength of the low-lying soda solution, either passes straight down or overflows into the second cylinder.

Working.—The water supply passes through a vertical turbine to the circumference of the distributor, thence over the circular weir, the circumference of which is properly subdivided, to the air vessel, the lime tank, and the soda tank. Alternately the water rises and sinks in the air vessel and drives the air into the lime tank, agitating the milk of lime; then the water in the air tank is

syphoned out and the action is repeated. The amount of water added to the lime regulates its supply, and can easily be altered by shifting the subdivision on the circular weir. The central cylinder of the soda tank is filled with soda

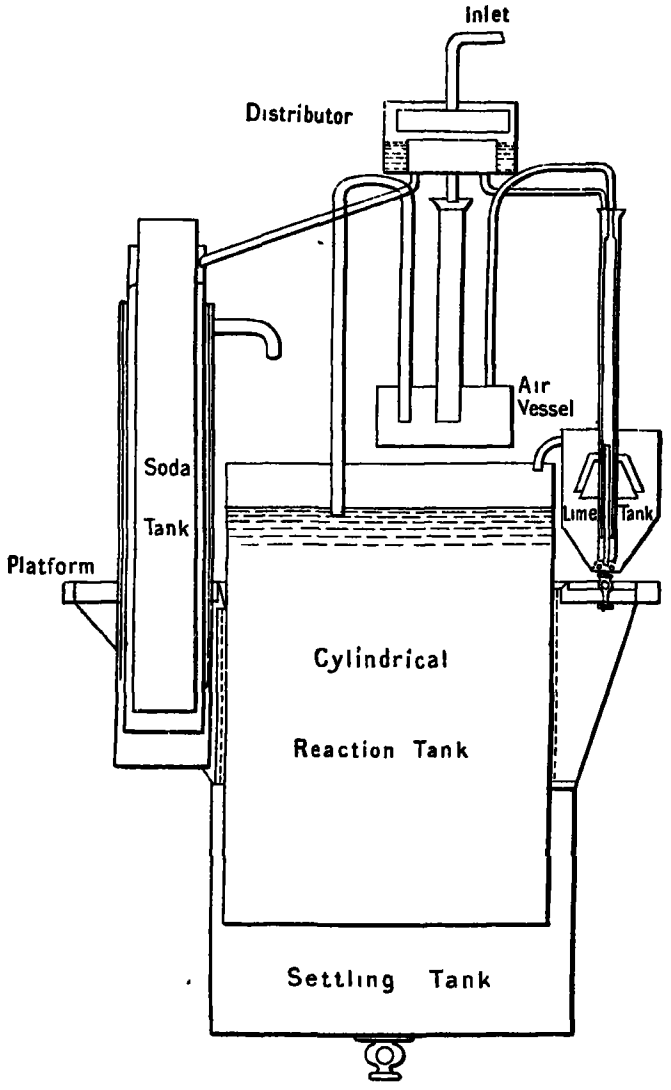


FIG. 76.—Harris Anderson water softener.

crystals, which partly dissolve in the water, the heavy soda solution settling at the bottom as shown A small, but constant, supply of water is run from the distributing weir into the second cylinder, passing through the dense fluid at the bottom and up outside the third cylinder. Should, however, this rising solution be very dense, then the added water will flow over the top of the second

cylinder and under the third cylinder. Thus, by adjusting the height of the second inner cylinder, a soda solution of a definite strength is obtained The sediment formed in the reaction chamber and in the settling tank is run out through a sludge cock

Paterson Exhaust Heater and Purifier.—Where exhaust steam is used

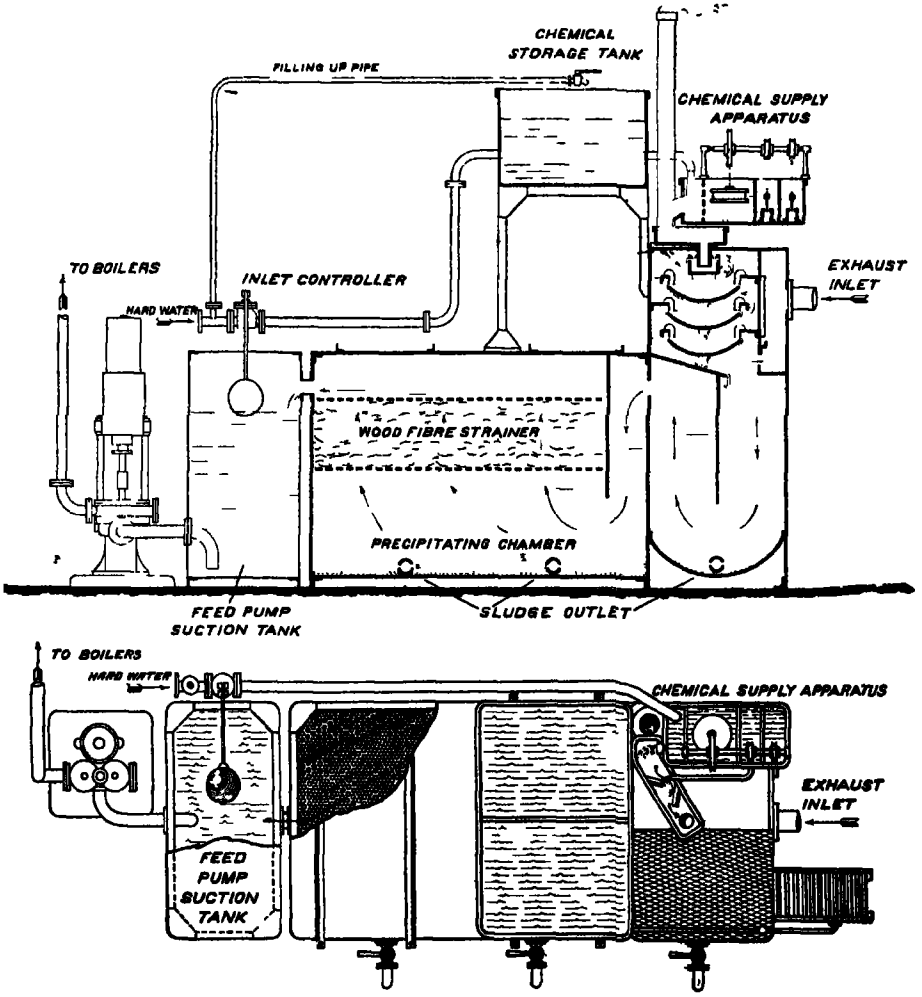


FIG 77.—Paterson's exhaust heater and softener.

for heating purposes in connection with water softening, it should be passed through some form of oil separator before entering the softener. The Paterson exhaust heater and purifier is interesting, in that it combines the removal of temporary hardness by means of steam with the simultaneous separation of the oil (fig. 77).

The hard water supply, controlled by the float in the feed-pump suction tank, enters the chemical supply apparatus, where it is measured continually in

its passage through a narrow vertical discharge weir, which makes the water level in this chamber very sensitive to variation in the amount passing A large float in an adjoining compartment controls the position of two long tapered valves which regulate the discharge of softening reagents. The level of the softening reagents above the tapered valve seats is kept constant by ball-cocks connected to the chemical storage tanks alongside The hard water and the reagents are thoroughly mixed in the horizontal mixing trough, and pass through a water seal into the heating chamber.

The exhaust steam enters on the right, and after passing through a preliminary grease separator, for the removal of the black oil, enters the heating chamber and passes through the trays in a counter-flow direction, finally escaping to the atmosphere.

The heating trays are constructed of light sheet steel, and can readily be withdrawn for heating purposes.

The water from the distributing box falls into the centre of the top tray. Owing to the great length of the trays the water overflows at the edges in exceedingly thin films, which cling to the under side of the trays, dropping from the centre into the middle of the tray immediately below After working its way to the edges of No 2 tray, it again overflows on the under side of the tray, and drops into the middle of No. 3, and so on. By this means the exhaust steam comes into film contact with the water and removes the temporary hardness without the aid of chemicals, by driving off the carbonic acid gas and precipitating the lime salts in and on the trays.

The reaction is as follows .—

$$Ca(HCO_3)_2 = CaCO_3 + CO_2 + H_2O.$$

For the removal of the permanent hardness, sodium carbonate is necessary, and by means of the chemical supply apparatus this is added in accurate proportion to the amount of water passing.

The heavy impurities are deposited in the heating chamber, and sludged to the drain The water then passes into the precipitating chamber, where the bulk of the impurities settle out, the purification being obtained by upward filtration through wood fibre The softened and purified water flows into the feed-pump suction tank

It is important to check the purity of the chemicals used, particularly in the case of lime Methods for testing both lime and sodium carbonate are given in Chapter XIX

In order to get good results with any type of water softener, it is important that the apparatus should not be worked beyond its capacity This is particularly important in the case of a lime and soda process, for the separation of the precipitate is not instantaneous J. W Wood (*J S.C.I.*, 1917, p 1256) studied this question very carefully with a water containing 25 parts of hardness per 100,000, illustrating the course of the action by the following experimental method The water to be softened is placed in a vessel about 1 foot deep and 5 inches in diameter, through which a powerful beam of light can be projected in a vertical direction by means of a reflector.

At first the water is perfectly clear and the beam is not visible as it passes through the water, nor are the conditions changed on adding the theoretical quantity of lime water The water remains clear for two or three minutes, after which a slight opalescence appears, which gradually becomes more marked until the vessel becomes filled with a milky fluid, but no individual particles can be seen After this stage the particles grow either by addition of fresh material

or by segregation, but, in any case, appear to become fewer in number and the mixture acquires the character of a true suspension with particles of appreciable size, the water between them being perfectly clear. After the particles have reached appreciable size they settle slowly, leaving the liquid clear. During the first three or four minutes, during which the water remains clear, the determined hardness corresponds with the sum of the original hardness and the added lime. If a little wet precipitate from a previous experiment be added, the precipitation becomes too rapid to detect any intermediate stages. Raising the temperature to 15° to 20° C. also increases the rate of action, as also does the addition of slight excess of lime. Filtration is also an important factor in accelerating the rate of precipitation.

With lime alone the time required for complete softening was found to be ninety minutes, and for lime and soda in correct proportions, fifty to sixty minutes This can be reduced to forty minutes by the use of more lime and soda, but, according to the author, the softening plant should be large enough to allow the full fifty minutes for the water to pass through.

The Permutit Process.—This method, which is to a large extent replacing the other forms described, depends upon the use of zeolites. These are hydrated silicates of aluminium with calcium or sodium They occur naturally, or may be manufactured artificially. Artificial zeolites containing sodium are termed "permutit," such as $Na_2O.Al_2O_3.2SiO_2.6H_2O$. When permutit is brought into contact with an aqueous solution of a salt of calcium or magnesium an exchange of sodium for the alkaline earth metal takes place If sufficient sodium permutit be present the whole of the calcium and magnesium are removed from the solution, an exactly equivalent quantity of the sodium salt of the acid remaining

This is illustrated by the equations

$$Na_2O.Al_2O_3\ 2SiO_2+Ca(HCO_3)=CaO\ Al_2O_3.2SiO_2+2NaHCO_3,$$
$$Na_2O\ Al_2O_3\ 2SiO_2+CaSO_4=CaO\ Al_2O_3.2SiO_2+Na_2SO_4$$

It should be noted that when temporary hardness is removed an equivalent amount of sodium bicarbonate is left in solution This for certain purposes has to be taken into account. To soften hard water it is simply allowed to percolate through a layer of permutit in the form of granules After a time the softening action ceases, owing to all the sodium having been replaced by calcium or magnesium with the formation of calcium or magnesium permutit.

The calcium permutit is now washed with a solution of sodium chloride, when sodium permutit is regenerated in accordance with the equation

$$CaO.Al_2O_3.2SiO_2+2NaCl=CaCl_2+Na_2O.Al_2O_3.2SiO_2.$$

The soluble calcium chloride is carried away with the salt solution. The residual salt and calcium chloride is washed away with soft water and the regenerated sodium permutit can now be used again. The process is capable of being continued indefinitely, subject only to wear and tear of the permutit.

An example of the plant used is shown in fig. 78.

Since each molecule of calcium or magnesium bicarbonate present in the original water gives rise to an equivalent of sodium bicarbonate, the alkalinity of the water may be high after softening. Though an absolutely "soft" water can be produced, the quantity of permutit required per thousand gallons, and also of salt for its regeneration, is considerable for very hard waters. For these reasons it is often more economical to combine the permutit process with precipitation. For example, the temporary hardness may be removed by means

of lime, leaving only the permanent hardness to be dealt with by the permutit. In this way, not only is the quantity of permutit and salt reduced, but the pres-

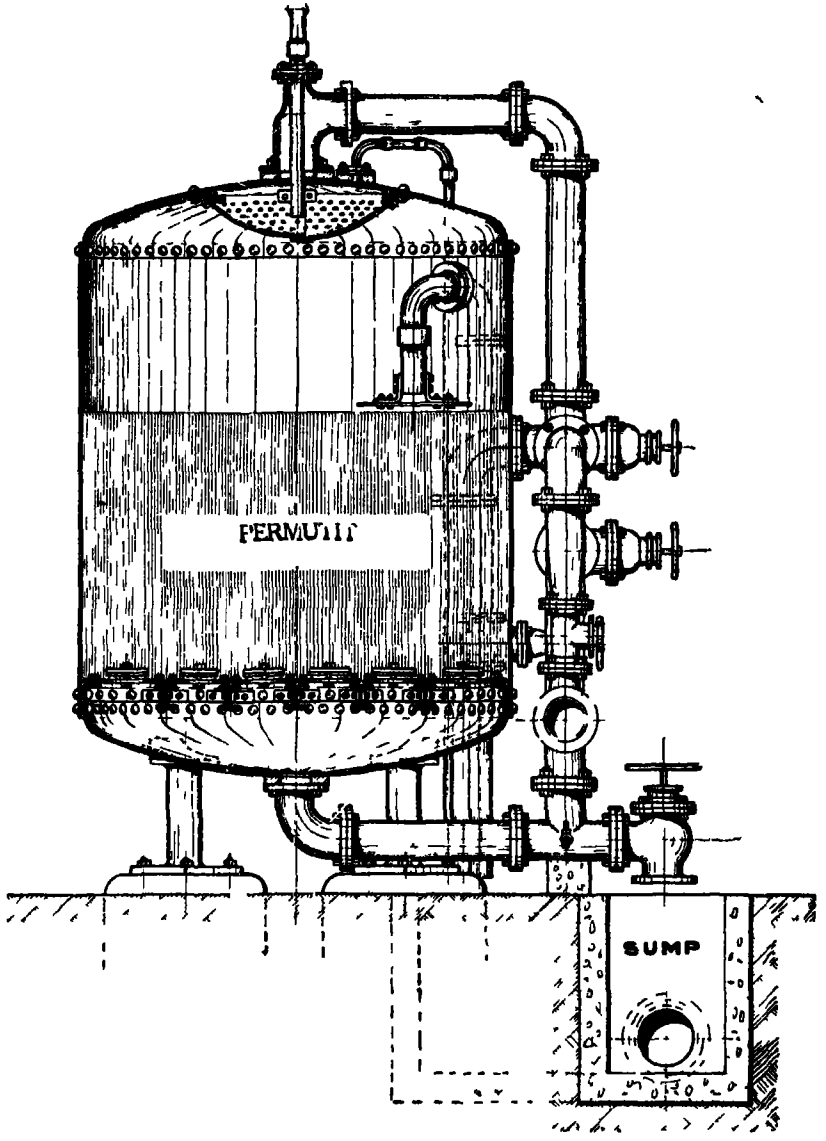


FIG. 78.—Permutit softener.

ence of sodium bicarbonate in the softened water is also avoided Such a combination is represented by the equations

$$CaH(CO_3)_2+CaO=2CaCO_3+H_2O,$$
$$Na_2Al_2O_32SiO_2+CaSO_4=CaOAl_2O_32SiO_2+Na_2SO_4.$$

Modified types of permutit may be used also for removing other impurities, such as free alkali and iron, from water For removing free alkali hydrogen permutit is employed, prepared by heating sodium permutit with an acid. The compound exchanges its hydrogen for sodium in an alkaline solution.

Iron may be removed from water by means of manganese permutit. If calcium permutit be treated with a solution of manganese chloride, a manganese permutit is produced of the composition $MnOAl_2O_3 2SiO_2$ Manganese permutit when treated with a solution of calcium permanganate exchanges its MnO for CaO, but at the same time an oxide of magnanese, $MnOMn_2O_7$, is precipitated on the surface of the permutit in an adherent form—

$$MnOAl_2O_3 2SiO_2 + Ca(MnO_4)_2 = CaOAl_2O_3 2SiO_2 + MnOMn_2O_7.$$

This compound contains available oxygen, which it gives up when water containing iron is passed over it. The iron is oxidised to insoluble ferric oxide, which remains on the surface of the permutit.

Permutit may also be made use of for the purification of polluted water. Organic matter is oxidised by adding to the water a slight excess of sodium or potassium permanganate. Some of the manganese is precipitated as an oxide, but some remains in solution. The latter is removed as manganese permutit as indicated above.

The Analysis of Industrial Water.

Determination of Hardness.—For industrial purposes, where only the "total hardness" is required, an approximate method, using "standard soap solution," is generally employed.

This depends upon the fact that when a solution of soap is added to a hard water no lather is produced on shaking until all the calcium and magnesium have been precipitated as insoluble soaps. When this has taken place, further addition of soap solution, followed by shaking, gives a permanent head or lather.

The following solutions are required for this test.—

1 **Standard Calcium Chloride.**—This is made in the following way. 0·2 grammes of Iceland spar is placed in a dish, dilute hydrochloric acid is added and the dish covered with a clock glass When the spar has dissolved, the clock glass is rinsed with distilled water, the washings being collected in the dish. The solution is then evaporated two or three times to expel hydrochloric acid, after which it is dissolved and made up to 1 litre Fifty c c of this solution contain calcium equivalent to 0·01 gramme of calcium carbonate.

2. **Standard Soap Solution.**—Twelve grammes of oleic acid are dissolved in industrial spirit and exactly neutralised with alcoholic potassium-hydroxide solution, phenolphthalein being used as indicator. The solution is then made up to 1100 c.c with 50 per cent industrial spirit After standing for a day it is filtered and standardised. For this purpose 50 c.c. of the standard calcium-chloride solution are placed in a stoppered bottle of about 100 c.c. capacity. The soap solution is then run in from a burette, 1 c.c. at a time, the stopper being replaced and the bottle well shaken after each addition. As soon as a temporary lather is observed, the soap solution is added carefully till, after shaking, the lather is permanent for two minutes. From the number of cubic centimetres of soap solution used, its strength in terms of calcium carbonate can be calculated. One litre is then diluted with 50 per cent. spirit to a convenient strength, say 1 c.c.=0·001 calcium carbonate.

In order to test the hardness of a sample of water, 50 c.c. of it are placed

in the stoppered bottle and titrated with the soap solution as described above. If 10 c.c. of soap solution are required to produce a permanent lather, we know that 50 c.c of the water contain $10 \times 0{\cdot}001$ gramme calcium carbonate Hence, the hardness is 20·0 per 100,000, *i.e.* 14 degrees of grains per gallon. If more than 15 c.c. of the soap solution are necessary the results cannot be relied on. In this case a smaller volume of the water must be used, making it up to 50 c.c. with distilled water.

The result obtained indicates the total hardness of the water.

The permanent hardness may be estimated in the following manner: One hundred c c. of the water are boiled in a beaker till about 70 c.c have been evaporated. The residue is washed into a 100 c c flask with freshly boiled cold distilled water (*i.e* free from carbon dioxide) After cooling, the contents of the flask are made up to the mark with the carbon-dioxide free water, mixed and filtered The residual permanent hardness is then determined in 50 c c of the filtrate If the result obtained be deducted from the total hardness, the temporary hardness is obtained.

The soap test is not accurate. It is useful for checking the hardness of a softened water, or for cases where a rapid, though approximate, result is necessary

For accurate results, hardness must be determined by a method depending on titration with standard acid. For temporary hardness, 100 c c. of the water are titrated with decinormal hydrochloric or sulphuric acid and methyl orange. Each cubic centimetre of acid used corresponds to 0·005 parts of hardness expressed as calcium carbonate.

The determination of temporary hardness by titration with acid, using methyl orange as the indicator, is rather difficult. The change of colour is not very sharp. This difficulty is overcome by using the method of Pfeifer and Wartha, in which alizarin is the indicator. But since alizarin is sensitive to carbon dioxide the titration must be carried out at boiling-point, or the liquid boiled after each addition of acid to expel carbon dioxide The following details are taken from Procter's *Leather Chemists' Pocket-Book* —

Temporary Hardness.—To 100 c c of the water a drop or two of 2 per cent. purest alizarin paste are added Decinormal acid is run in till the violet colour changes to lemon yellow. The solution is then boiled. As soon as the carbon dioxide is expelled the violet colour reappears The boiling solution is now titrated with the decinormal acid till the lemon colour is permanent after boiling. This indicates that all the temporary hardness has been neutralised. The hardness is calculated from the volume of acid in the usual way

Permanent Hardness.—One hundred c c. of the water are pipetted into a hard glass flask, and 10 c.c of decinormal sodium hydroxide and 10 c.c of decinormal sodium carbonate are added The contents of the flask are then boiled gently for about half an hour to precipitate the temporary, and decompose the permanent, hardness The calcium salts are precipitated as carbonates and magnesium salts as hydroxides The concentrated residue is now filtered into a flask, the paper being washed with boiled distilled water The filtrate is cooled and titrated with decinormal acid and methyl orange Each cubic centimetre of decinormal alkali which has disappeared corresponds to 0·005 grammes of permanent hardness expressed as calcium carbonate. The determination may be checked by dissolving the precipitate on the filter-paper in excess of decinormal acid, boiling to expel carbon dioxide, and then titrating back. This will give the total hardness.

Filtration may be avoided by the following modification of the process: After boiling, as described above, the mixture is washed into a stoppered 250 c.c.

flask with boiled distilled water, and allowed to cool. Sufficient cold carbon-dioxide free-distilled water is then added to bring the volume up to 250 c.c., the contents of the flask well mixed and allowed to stand till the precipitate has settled. Fifty c c. of the clear solution are then withdrawn by means of a pipette, and the residual alkali is determined by titration.

Hardness due to Magnesium.—It is often desirable to know how much of the hardness is due to magnesium; for water softening it is essential. Magnesium hardness may be determined, also, by Pfeifer's method.

One hundred c.c. of the water are accurately neutralised with decinormal hydrochloric acid, and boiled till the carbon dioxide is expelled. The residue is washed into a 200 c.c. flask and mixed with 100 c c of filtered lime water. The mixture is heated in boiling water to complete the precipitation of the magnesia, cooled, and made up to the mark with carbon dioxide free water. The contents of the flask are well mixed and allowed to stand till the precipitate has settled. Fifty c.c are then withdrawn with a pipette and titrated with decinormal acid and phenolphthalein. The value of the lime water in terms of decinormal acid must also be determined From the quantity of lime which has disappeared the magnesium hardness can be determined. The reactions involved are—

$$MgCl_2 + Ca(OH)_2 = Mg(OH)_2 + CaCl_2,$$
$$MgSO_4 + Ca(OH)_2 = Mg(OH)_2 + CaSO_4.$$

Example.

Fifty c c of the lime water require 22 5 c.c N/10 acid. One hundred c c of the mixture require 20 1 c c N/10 acid

Therefore 22 5 − 20·1 = 2 4 c c N/10 acid correspond to the magnesium hardness in 50 c c. of the original water In terms of calcium carbonate the hardness is 2 4 × 0 005 in 50 c c of water

Anderson's process for the determination of hardness caused by magnesium is somewhat simpler than that just described, and is particularly suitable for the examination of softened water. The following details are taken from Anderson's paper (*J S C I.*, 1915, p. 1180) —

In order to calculate the correct quantities of lime and sodium carbonate to use for softening a water, we must determine the following data. (1) Free carbon dioxide, (2) alkalinity or carbonate hardness, (3) total lime, (4) total magnesia.

Free carbonic acid is estimated by titration with sodium carbonate and phenolphthalein as already described.

Total hardness is next determined in the following way: One hundred c c. of the water are made slightly acid with hydrochloric acid, and concentrated to about 30 c c. and washed into a graduated 100 c.c flask Methyl orange is added, and the liquid is exactly neutralised with N/10 alkali Ten c.c. of decinormal sodium hydroxide and also of decinormal sodium carbonate are now added, and the mixture is boiled for two or three minutes to precipitate the calcium and magnesium The flask and its contents are then cooled, made up to the mark with cold carbon-dioxide free water, and filtered. The alkali in the filtrate is then titrated to obtain the total hardness. In the determination of *magnesium hardness*, advantage is taken of the fact that magnesium can be completely precipitated as magnesium hydroxide by cold sodium-hydroxide solution in the absence of carbon dioxide. One hundred c.c. of the water are acidified and concentrated as described above. The concentrated residue is washed into a stoppered cylinder and exactly neutralised. After neutralising,

10 c.c. of N/10 sodium hydroxide are added, followed by carbon dioxide free-distilled water to bring the volume back to 100 c.c. The stopper is then inserted and the contents of the cylinder are well mixed After standing till the precipitated magnesium hydrate has settled down, a portion of the clear supernatant liquid is pipetted out and the residual sodium hydrate determined by titration. The magnesium hardness is calculated from the sodium hydroxide that has disappeared, either in terms of calcium carbonate or magnesia as desired. The calcium hardness is obtained by deducting the magnesium hardness, expressed as calcium carbonate, from the total hardness. From these data the quantities of saturated lime water and soda ash required for softening are obtained by means of the following formulæ:—

Temporary hardness $\times 0{\cdot}62$ = percentage of lime water, *i e* volume per 100 parts of water.
Temporary magnesium hardness $\times 1{\cdot}24$ = percentage of lime water.
Permanent calcium hardness $\times 0{\cdot}15$ = lbs of soda ash per 1000 gallons.
„ magnesium hardness $\times 0{\cdot}62$ = percentage of lime water.
„ „ „ $\times 0{\cdot}15$ = lbs of soda ash per 1000 gallons.

Newland's method for estimating hardness (*J S.C I*, 1916, p 445) has many interesting features. It is carried out in the following manner:—

1. *Temporary Hardness.*—To 100 c.c. of the water add 2 c c. of methyl-red solution. Then add decinormal acid till a light red colour appears. Now boil to expel carbon dioxide. Add more decinormal acid, boiling after each addition till the colour no longer disappears. Methyl red is yellow in neutral solution, but red at a hydrion concentration of 10^{-5} or 1/100,000N Methyl orange does not become red till the acidity is ten times greater, *i.e.* about 10^{-4}N Moreover, the end point is not sharp with decinormal solutions, and cannot be seen in artificial light. Methyl red is also better in the presence of ammonia It is, however, very sensitive to carbon dioxide, which must be removed by boiling The indicator is made by dissolving 0·05 gramme of the dye in a litre of 80 per cent. spirit. In determining temporary hardness the trouble of constant boiling may be avoided by adding excess of decinormal acid, boiling to expel all the carbon dioxide, and then titrating back with decinormal sodium-hydroxide solution

2. *Permanent Hardness* —To 100 c c of the water add 10 c.c of N/25 potassium-carbonate solution and evaporate to dryness on the water bath The residue is mixed with 10 c c of 20 per cent alcohol, warmed on the water bath and filtered The dish and filter are then washed four times with 90 per cent alcohol. The filtrate is titrated as above The precipitate remaining in the dish and on the filter is used for the determination of total hardness. Magnesium and calcium carbonates are insoluble in 90 per cent alcohol Potassium carbonate is more soluble in alcohol than sodium carbonate.

3 *Total Hardness.*—This may be determined by dissolving the precipitate (2) in excess of decinormal acid, boiling and titrating back. Or it may be found from the sum of the temporary and permanent hardness, or by neutralising 100 c c. of the water as in the determination of temporary hardness and evaporating with potassium-carbonate solution, and proceeding as in the determination of permanent hardness. The method can also be extended to the determination of calcium and magnesium. Calcium carbonate dissolves in a large excess of ammonium carbonate, but is re-precipitated on boiling. At ordinary temperatures magnesium carbonate is not precipitated, but is on boiling. With excess of ammonium carbonate the precipitate dissolves, and is

not thrown down on boiling. That is, magnesium salts give no precipitate with excess of ammonium carbonate, even on boiling. Hence we may determine the hardness due to calcium by evaporating the water with ammonium-carbonate solution and extracting the magnesium carbonate The difference between the total hardness and that due to calcium is the hardness produced by magnesium. The operation is conducted as follows: One hundred c.c. of water are evaporated with 10 c c. of a 2 per cent. solution of ammonium carbonate. The residue is mixed with 15 c.c. of the same solution and warmed for two minutes. The liquid is filtered by decantation and the residue extracted twice with 10 c.c. of the reagent. The basin is rinsed four times with 90 per cent. alcohol, and the filter is washed with the same spirit till it is free from alkali, using methyl red as indicator. The residual calcium carbonate is then dissolved in excess of decinormal acid and titrated back after boiling off carbon dioxide

Testing Softened Water.—Anderson (*loc. cit.*) gives the following method for checking softened waters: It is necessary to determine (1) total hardness by the soap test, (2) alkalinity to phenolphthalein, and (3) total alkalinity to methyl orange. The figures thus obtained are interpreted as follows: The phenolphthalein figure is multiplied by 2, and the total alkalinity subtracted from the result. If there is a positive remainder, caustic alkalinity is present, and the remainder is caustic alkalinity in degrees If there is no remainder, only carbonate alkalinity is present, whilst if the remainder is negative, the interpretation is that bicarbonate alkalinity is present to an amount, in degrees, numerically equal to the remainder.

If the amount of soda added in the softener has been correct, the hardness and the total alkalinity will be the same, if the soda is in excess, the total alkalinity exceeds the hardness, and if deficient, the hardness exceeds the total alkalinity.

If the quantity of lime added has been correct, the phenolphthalein figure will slightly exceed one-half the total alkalinity, *i e.* a slight amount of caustic is present If lime is deficient, the phenolphthalein figure is less than one-half the total, or bicarbonate is still present, and if excess of lime has been used, the phenolphthalein figure will decidedly exceed one-half the total

Any errors of treatment disclosed by these tests are also presented in a quantitative form, so that the exact alteration necessary can be calculated. These points are illustrated by the following examples. The original water contained about fifty-four degrees of hardness, and was highly magnesian The two softened samples are both slightly above the minimum point, but the explanation in the two cases is different.

	No 1	No. 2
Hardness . . .	8 0°	8 1°
Phenolphthalein alkalinity . . .	2 5°	3 9°
Total alkalinity . .	9 0°	6 0°

In No 1 lime is deficient, 4° as bicarbonate being still present, doubtless mainly magnesium bicarbonate. Hence $4{\cdot}0\times1{\cdot}24=5$ per cent additional lime water is required No. 2 is 2° deficient in soda The caustic indication is 1·8°, hence the lime is correct, as the water is magnesian, and $2{\cdot}0\times0{\cdot}15=0{\cdot}3$ lb. of soda ash per 1000 gallons additional is required

An example of a good softened water is—hardness, 4·0°; alkalinity (phenolphthalein), 3·0°; total alkalinity, 4·0°. The volume of N/10 acid, using 100 c.c. of water multiplied by 3·5, gives the alkalinity. Caustic alkalinity, 2·0°. The average of thirty consecutive tests taken five times daily for six days gave—hardness, 4·8°; alkalinity (phenolphthalein), 4·4°; total alkalinity, 5·9°.

These indicate, on the whole, a trifling excess (1·1°) of soda ash, and caustic, 2·9°, also rather on the high side, but hardly so much as to call for any alteration.

The Determination of Iron.—Iron may be estimated by concentrating 500 c c. of the water acidified with hydrochloric acid to about 25 c c. This residue is washed into a graduated cylinder and made up to a definite volume, *e.g.* 50 c.c with distilled water. One c.c. of a dilute freshly prepared (1 to 2 per cent) solution of potassium ferrocyanide is then added. A blue colour due to the formation of prussian blue is produced, the depth of which is proportional to the amount of iron in the water. This colour is now matched with a standard solution of iron. About 25 c.c. of distilled water, 1 c.c. of hydrochloric acid, and 1 c.c. of potassium-ferrocyanide solution are placed in a second similar cylinder A solution containing 0·001 gramme of iron per c.c. is then carefully added with stirring till the colour is the same in both cylinders. The volume of the standard iron solution used gives the quantity of iron in the first solution, *i e* in the 500 c c of the original water. A standard iron solution may be prepared by dissolving 1 gramme of pure iron wire in hydrochloric acid and evaporating to dryness with a little nitric acid to oxidise the ferrous chloride The residue is dissolved in dilute hydrochloric acid and made up to 1 litre. Or 7 grammes of ferrous ammonium sulphate may be dissolved in water and oxidised with nitric acid

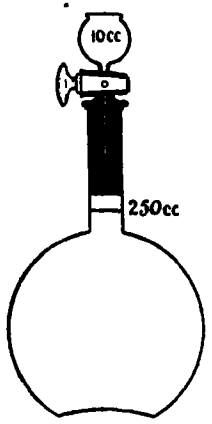


FIG 79.—Friend's apparatus

Dissolved oxygen in water can be estimated by Winkler's process. A stoppered bottle of known capacity is filled to the stopper with water. By means of a pipette, 1 c c of a cold saturated solution of manganese chloride is introduced at the bottom of the bottle, followed in the same manner by 3 c.c. of 33 per cent. sodium-hydrate solution containing 10 per cent. of potassium iodide. At first manganous oxide, MnO, is precipitated. In the presence of dissolved oxygen this is rapidly oxidised. The stopper is replaced and the contents of the bottle mixed to complete the reaction Sufficient hydrochloric acid (about 5 c.c.) is then introduced, when iodine equivalent to the dissolved oxygen is liberated. The contents of the bottle are now poured into a flask and the iodine is titrated with centinormal thiosulphate solution, using starch solution as indicator, at ordinary pressure and temperature. Each cubic centimetre of centinormal thiosulphate corresponds to 0·00008 gramme of dissolved oxygen. Water, when saturated, contains 1 part per 100,000 of dissolved oxygen.

There is some difficulty in the manipulation of Winkler's process when using an ordinary stoppered bottle. This may be overcome by means of a flask devised by J. N. Friend (*Analyst*, 1925, p. 248), illustrated in fig. 79.

Using the apparatus as shown in sketch, it is possible to overcome entirely the two main difficulties of such determination, *i.e.* those of (*a*) closing the apparatus after filling with water, and (*b*) opening the apparatus and adding the necessary acid to stop further oxidation without admitting some air. Using Winkler's method, the flask is filled to the 250 c.c. mark with water and approximately 1 c.c. of solution added, containing 33 grammes NaOH and 10 grammes KI per 100 c.c. About 2 c.c. of solution containing 4 grammes $MnCl_2.4H_2O$ per 100 c.c. are now added, sufficient to raise the level above the lower end of the stopper and to fill the capillary tube when the latter is pushed home. On

closing the tap the apparatus is sealed to the entire exclusion of air. After the reaction has taken place, some 5 c.c. concentrated HCl are added to the funnel, the tap opened and stopper withdrawn slowly The acid passes down the capillary and stops further reaction in the flask before air can gain access. A rubber stopper may now be inserted, and, after shaking and standing for five minutes, the liberated iodine is estimated in the usual manner.

Determination of Free Carbon Dioxide.—Pettenkofer's method gives both free carbon dioxide and loosely combined carbon dioxide as bicarbonates. The free carbon dioxide may be titrated with sodium carbonate and phenolphthalein, since sodium bicarbonate is acid to this indicator while the normal carbonate is alkaline. In Pettenkofer's method a known volume of water is placed in a stoppered flask, together with a little strong barium-chloride solution and some ammonium chloride. The contents of the flask are then made up to a definite volume with standard baryta water, the stopper inserted and the flask shaken. When the precipitate of barium carbonate has settled down, a portion of the clear liquid is withdrawn with a pipette and titrated with decinormal acid The amount of barium hydrate required to combine with the carbon dioxide is thus found in terms of decinormal acid, each cubic centimetre of which is equivalent to 0·0022 gramme. According to Tillmans and Heublein (*J S.C.I*, 1917, p. 938), the precipitated barium carbonate occludes or absorbs barium hydrate, thus rendering the titration inaccurate. The presence of salts of magnesium also affects the accuracy of the process. They recommend the following method of titration.—

One c.c. of 0·0375 per cent. phenolphthalein solution is added to 200 c.c. of water contained in a stoppered flask. This is titrated with N/20 sodium-carbonate solution till a pink colour is obtained, which persists for five minutes. If, at the end of the titration, more than 440 mgm. of carbon dioxide in the form of bicarbonates is present, the sample must be diluted with carbon-dioxide free-distilled water and titrated again. This is because the reaction of sodium bicarbonate towards phenolphthalein depends upon the relative concentration of the two bodies. It is acid to small quantities of the indicator and alkaline to large quantities. The quantity of the indicator present should be proportional to the amount of sodium bicarbonate. Czensny (*J.S C I.*, 1919, 476A) adopts the following method of titration to overcome this difficulty: One hundred c.c. of the water are titrated with a solution containing 2·6525 grammes of sodium carbonate and 2·5 grammes of phenolphthalein per litre till a permanent pink colour is produced. From the volume used 0·52 c.c. is deducted. The remainder multiplied by 1·22 gives the free carbon dioxide in milligrammes per 100 c.c. of water.

Suspended Matter.—After mixing the water thoroughly, 500 c.c. are poured off rapidly before the suspended matter settles and passed through a weighed Gooch filter. The residue on the Gooch is dried at 100° C. and weighed. Good waters do not often contain suspended matter, though it is frequently present in streams and surface waters.

If a platinum or silica Gooch has been used, it may be ignited to burn off the organic matter and reweighed. The suspended matter is thus separated into organic and inorganic constituents The latter may be dissolved and examined. The approximate nature of the organic matter is ascertained by a microscopic examination of some of the freshly collected suspended matter.

Total Dissolved Solids.—From 50 to 250 c.c. of the filtered water are evaporated to dryness on the water-bath in a weighed dish. The residue is dried at about 105° to 110° C. and weighed.

Chlorine as Chlorides.—One hundred c c. of water are placed in a porcelain dish. A drop or two of potassium chromate solution are added and decinormal silver nitrate is run in from a burette with stirring till a faint red colour is obtained Each cubic centimetre of silver nitrate used corresponds to 0·00355 grammes of chlorine. An organically pure water should not contain more than 2 parts of chlorine per 100,000. Larger quantities may be permitted if their presence can be explained satisfactorily The chlorine content of a water is remarkably constant. Any sudden rise would be suspicious and its cause demand careful investigation.

Nitrogen as Nitrate.—Many methods are used for this determination. That depending upon the use of phenoldisulphonic acid is the simplest, and is quite satisfactory for most purposes A solution of phenoldisulphonic acid is prepared as follows :—

Eighty c c. of phenol are mixed with 200 c.c. of concentrated sulphuric acid and heated on the water-bath for eight hours. After cooling, 140 c.c. of strong hydrochloric acid are added.

A standard solution of potassium nitrate is also required. If 0·7423 gramme be dissolved in a litre of water, each cubic centimetre will contain 0·001 gramme of nitrogen. The estimation is carried out in the following manner —

From 10 to 50 c.c of the water, depending upon the quantity of nitrate present, are mixed, with constant stirring, with 1·5 c.c. of strong sulphuric acid and then with 2 c c. of phenoldisulphonic acid. The mixture is concentrated on the water-bath to about 10 c c. at a temperature not exceeding 70° C. This residue, containing the nitrogen as picric acid, is washed into a graduated cylinder or flask, rendered alkaline with ammonia or potassium hydroxide, and made up to 100 c.c. At the same time a measured quantity, say 10 c.c of the standard nitrate solution, is treated in exactly the same manner. The solution having the deeper yellow tint is then diluted till its colour is the same as that of the other From the dilution necessary the quantity of nitrate present can be calculated. Much trouble is saved by using a set of yellow glasses and a Lovibond or other form of tintometer. The glasses are standardised once for all against the standard nitrate solution. Pure waters contain very little nitrogen as nitrate. In the case of surface waters the amount may be as high as 0·5 parts per 100,000. Waters collected from polluted subsoil may contain large quantities, reaching sometimes from 3 to 5 parts per 100,000. Such large amounts as this are objectionable in a water either for steam raising or bleaching.

Determination of Organic Matter.—The organic purity of a water may be judged by determining (1) the saline and protein ammonia, and (2) the amount of oxygen which it can absorb and the rate of absorption. For most purposes the estimation of free or saline and protein ammonia is sufficient.

The following solutions are required —

1. A standard solution of ammonium chloride containing 3·147 grammes per litre. This is diluted for use to 1 in 10. Each cubic centimetre of the diluted solution contains 0·0001 gramme of ammonia.

2. *Nessler Solution.*—This is mercury potassium iodide, $HgI_2 2KI$, dissolved in caustic potash In presence of traces of ammonia it gives a brown colour, the depth of which is proportional to the amount of ammonia present With large quantities of ammonia a brown precipitate is produced. The solution is made as follows .—

Dissolve 35 grammes of potassium iodide in 100 c.c. of distilled water and add to it a cold solution containing 16 grammes of mercuric chloride in about 300 c.c. of distilled water. A slight permanent precipitate will be produced,

The mixture is then made up to 1000 c.c. by the addition of a 20 per cent solution of sodium hydroxide.

This solution should be prepared some days before use, as, when freshly prepared, it is not always sensitive. Its sensitiveness should be carefully tested from time to time. It may be conveniently stored in a bottle fitted with a rubber bung through which passes a 2 c c. pipette, as shown in fig. 80. The required quantity can in this way always be obtained without any danger of sucking the solution into the mouth or disturbing the sediment, which a layer of broken glass will also help to keep down. The sensitiveness of Nessler's solution increases with keeping, and, when used, three minutes should be allowed for the development of the full tint.

Alkaline Permanganate Solution.—Powder finely 8 grammes of potassium permanganate and add it little by little, with constant stirring, to about 200 c.c. of boiling water in a beaker, place on a sand-bath, and boil gently for a few minutes to ensure complete solution. In a separate vessel dissolve 120 grammes of sodium hydrate in water, mix the two solutions together, and make up to about 1200 c c. to allow for subsequent concentration. Place the solution in a large retort or distilling flask connected with a condenser and distil until 50 c c of the distillate no longer give any colour on standing for three minutes with 2 c c. of the Nessler solution. Then cool, and pour into a stoppered bottle.

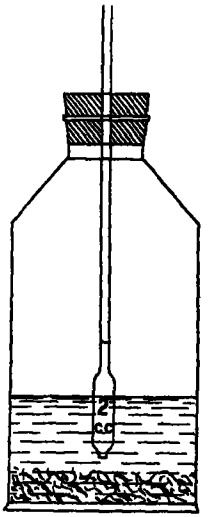


FIG. 80

Ammonia-free Distilled Water.—The water used for dilution should, of course, be ammonia free, and even laboratory distilled water rarely fulfils this condition unless freshly distilled. If 50 c.c. of it, after standing for three minutes in a covered vessel with Nessler's solution, give no coloration it may be safely used; if not, some must be distilled with a pinch of ignited sodium carbonate, rejecting the distillate so long as it affects Nessler's reagent and then storing in a carefully stoppered bottle.

Determination of Free Saline Ammonia.—Five hundred c.c. of water are placed in a distilling flask of about 1½ litres capacity, connected with a suitable form of condenser and boiled until the distillate no longer gives any coloration with Nessler's solution. Unless the apparatus is in constant use this preliminary cleansing must never be omitted. A very useful form of condenser, both efficient and economical in space, is the "Cribb," as shown in fig. 81. Having freed the apparatus from ammonia the water is poured away and 500 c c of the sample under examination introduced, together with a pinch of ignited sodium carbonate. One hundred c.c. are distilled off, well mixed, and 50 c.c. poured into a glass cylinder of about 100 c.c. capacity, 2 c c. of Nessler solution are then added, and the colour at the end of three minutes observed.

Into a second Nessler cylinder a small quantity (say 5 c.c.) of the diluted standard ammonia solution is run in from a burette, made up to 50 c.c. with ammonia-free distilled water, and 2 c.c of Nessler solution added. After allowing three minutes for the colour to develop, the two cylinders are placed side by side upon a white porcelain tile and the colours compared by looking vertically down through the liquid. If the two tints are identical, the quantities of ammonia in the two cylinders are the same, *i.e.* equal to 0·00005, and this multiplied by 2

gives the amount present in the original 500 c.c. of water. If the colours of the two solutions are not identical, fresh trials must be made with varying quantities of the ammonium-chloride solution until the colour is matched. It will not do to add more ammonium chloride after the Nessler solution, but the experiment must be begun anew each time. While Nesslerising the first distillate a further 50 c c. are distilled off and tested in the same way. It will generally be quite free from ammonia, but if any be found the distillation must be continued till the distillate is free, the quantities being added to that obtained in the first experiment.

Protein Ammonia.—Fifty c.c. of the alkaline permanganate solution are now added to the contents of the flask, the distillation continued, and the ammonia estimated in exactly the same way as described above. It is well to mix thoroughly the permanganate by a rotary movement of the flask before commencing the distillation, or bumping will often ensue.

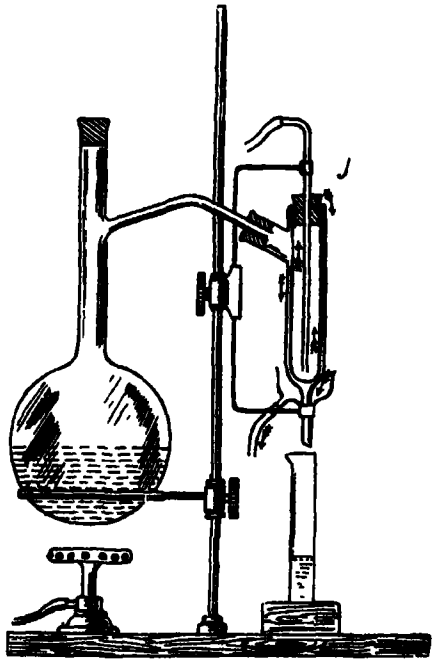


FIG. 81

Much time may be saved by using Lovibond's tintometer instead of matching the colour with ammonium-chloride solution.

The Nesslerised solution to be tested is placed in a half-inch cell and its colour matched with a series of glasses corresponding to definite quantities of ammonia.

The determination of ammonia is an important one, since excess of this constituent practically always indicates sewage pollution, especially if accompanied by chlorides and nitrates. Polluted water will generally contain putrefying organisms whose introduction is always undesirable. In general terms any water that contains more than 0·025 part of either free or proteid ammonia should be viewed with suspicion.

Oxygen Absorbed.—This process when taken in conjunction with the free and albuminoid ammonia gives valuable data upon which an opinion may be based. It gives the amount of organic matter in solution in terms of the oxygen required to oxidise it. Further, it enables us to distinguish between the readily oxidisable first decomposition products and the more complex organic bodies, since the former, at ordinary temperatures, are very rapidly oxidised and the latter only slowly. In contact with oxidisable matter potassium permanganate readily gives up its oxygen, especially if sulphuric acid be present, in accordance with the equation

$$K_2Mn_2O_8+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O.$$

The completeness of the oxidation of the organic matter varies with the temperature, the process only approaching quantitative exactness at 100° C.

It is therefore very necessary that standard directions should be followed or comparable results will not be obtained.

The particular temperature generally adopted is 80° F., in accordance with the recommendations of the Society of Public Analysts. The following solutions are necessary:—

1. Potassium permanganate, of which 1 c.c. contains 0·0001 gramme of available oxygen made by dissolving 0·396 gramme of pure potassium permanganate in a litre of distilled water.
2. Sodium thiosulphate, containing 1 gramme per litre of $Na_2S_2O_3$.
3. Potassium-iodide solution of 10 per cent. strength.
4. Dilute sulphuric acid (1 : 3).
5. Starch solution made by making 2 grammes soluble starch into a thin cream with water and pouring, with stirring, into 100 c.c. of boiling distilled water.

The determination is carried out as follows:—

Oxygen Absorbed in Fifteen Minutes.—One hundred c c. of the water are placed in a stoppered bottle of about 250 c.c. capacity and 100 c c. of distilled water in a second exactly similar bottle. Ten c c. of potassium-permanganate solution and 10 c.c. of dilute acid, both at a temperature of 80° F., are now measured into the two bottles, which are then placed in a water-bath maintained at a temperature of 80° F. and allowed to stand for fifteen minutes. If during this time the colour fades, a further 10 c c. of permanganate is added to each bottle. At the end of the fifteen minutes the bottles are well cooled and about 10 c.c. of potassium-iodide solution are added to each bottle, when the unused permanganate will liberate its equivalent of iodine, as shown by the equation

$$2KMnO_4+8H_2SO_4+10KI=6K_2SO_4+2MnSO_4+8H_2O+5I_2.$$

The iodine dissolves in the excess of potassium iodide, forming a brown or yellow solution. The standard sodium-thiosulphate solution is now run in from a burette, the stopper being carefully replaced and the bottle shaken after each addition until the colour has nearly disappeared. A few drops of starch solution are then added and the titration continued until the blue colour is just destroyed. From the difference between the number of cubic centimetres of thiosulphate used by the distilled water and materials and by the sample, the amount of decomposed permanganate or absorbed oxygen can be calculated.

If x be the number of cubic centimetres of thiosulphate required by the blank experiment, *i.e.* by 10 c.c. of permanganate and acid, then x c.c. of thiosulphate are equivalent to 0·001 gramme oxygen, and 1 c.c. of thiosulphate is equivalent to $0{\cdot}001/x$ gramme of oxygen. Now if y be the volume of thiosulphate used for the sample, then $(x-y)\times 0{\cdot}001/x$ is the quantity of oxygen absorbed by the volume of the water taken in the experiment.

Oxygen Absorbed in Four Hours.—This is determined exactly as described above, only the bottle is allowed to stand in the water-bath for four hours instead of fifteen minutes. It must be looked at from time to time and more permanganate added if the colour has faded. The above method may be much simplified without any loss of accuracy by titrating the permanganate directly with a standard solution of ammonium ferrous sulphate made by dissolving 4·90 grammes of the salt in 975 c.c. of water and adding 25 c.c. of sulphuric acid, making up to a litre when cold.

The solution should be kept in the dark and freshly made every three months. After the bottle containing the water and permanganate is taken from the bath the permanganate is titrated directly by adding the ammonium ferrous sulphate

from a burette till the colour is just destroyed, or, in a better method, is added to each bottle in excess, say 20 c.c., and then titrated back with the permanganate solution till the pink colour is just permanent. The calculation is then carried out as follows —

(*a*) Blank experiment—
20 c.c. of ammonium ferrous sulphate added.
10·0 c.c permanganate solution required.
(*b*) Sample—
20 c.c. ammonium ferrous sulphate added.
10·5 c.c permanganate used.
∴ Oxygen consumed=0·5×0 0001 gramme.

A good water should not absorb more than 0·05 oxygen in fifteen minutes nor more than 0·10 in four hours per 100,000 parts. The following modification of the absorbed oxygen test recommended by the Commission on Sewage Disposal gives valuable information in the case of polluted river water. The oxygen absorbed is determined as before, and a clean bottle is then completely filled with the water, stoppered, and placed in a cool incubator for a week, after which the oxygen absorbed is again measured. Badly polluted waters or those not properly aerated show an increase in oxygen absorbed after incubation.

The complete oxidation of the organic matter present in water generally requires a longer time than four hours at the temperature selected—80° F. The oxidation can be made much more rapid and complete by raising the temperature to the boiling-point for ten minutes In the presence of much chloride the results are too high, owing to the fact that the liberated hydrochloric acid decomposes permanganate at a high temperature.

$$2NaCl+H_2SO_4=Na_2SO_4+2HCl$$
$$K_2Mn_2O_8+16HCl=2KCl+2MnCl_2+8H_2O+5Cl_2.$$

On this account, if the chlorides are high, an alkaline solution of permanganate is often used. The following method (Pearmain and Moor, *Water*, p. 72) combines both determinations —

One hundred c.c. of water is placed in two conical flasks and 50 c.c. in two others To one of the flasks containing 100 c c. is added 10 c c of sulphuric acid (1 4), 5 c.c being also added to one of the flasks containing 50 c.c. To the other two flasks are added 10 and 5 c c respectively of a saturated solution of sodium bicarbonate Ten c.c. of a 0·5 per 1000 solution of permanganate is then added to each flask and the whole are boiled for ten minutes. The flasks are then cooled and the alkaline solutions acidified with 20 and 10 c.c. respectively of sulphuric acid 1 : 2 solution. Ten c.c. of ammonium ferrous sulphate containing 10 grammes of sulphuric acid and 10 grammes of the salt per litre are introduced and the solution titrated with the permanganate until a faint pink colour is produced. The difference between the results of the 100 c c and 50 c.c. in each case gives the figure for the permanganate required for the oxidation of the organic matter in acid and alkaline solution respectively. The permanganate solution is titrated with pure crystallised oxalic acid.

There is much to be said for the double determination, since organic bodies often behave quite differently with acid and alkaline permanganate solutions. It must always be remembered that "absorbed oxygen" results cannot be compared with one another unless the methods used are identical in all respects In stating results the method used should be specified, and that selected should, if possible, be the one in general use.

Ultimate Analysis of the Dissolved Solids.—From half a litre to a litre of water, according to the quantity of total solids present, is acidified with HCl and evaporated to dryness in a large platinum dish on the water-bath It is then moistened with dilute hydrochloric acid and again thoroughly dried to decompose the last traces of silicic acid. Upon extraction with dilute hydrochloric acid the silica remains insoluble and is carefully filtered off, washed, and dried. When dry the filter is folded and placed in a weighed platinum dish and ignited, the precipitate being far too small to detach. Deducting the weight of the filter ash we obtain directly the weight of the silica

Iron and Alumina.—The filtrate is rendered alkaline with ammonia and placed upon the water-bath for some time to complete the precipitation of the ferric hydrate and alumina. The precipitate is then filtered off, washed, dried, and weighed in the same manner as the silica. The amount is generally so small that a separation is unnecessary.

The iron is best determined on a fresh portion of water by evaporating to dryness with a little nitric acid, extracting the solids well with water and adding to the solution, in a Nessler cylinder, a few drops of potassium-ferrocyanide solution, when a blue solution will be produced proportional in depth to the quantity of iron present A standard solution of iron is made up so that each cubic centimetre is equivalent to 0·001 gramme of ferric oxide. This is made by weighing the necessary quantity of pure iron oxide, dissolving it in *aqua regia*, evaporating to dryness to expel chlorine, and finally making up to a litre with dilute acid A known volume of this solution is run from a burette into a Nessler cylinder, water added until the volume is the same as that in the first, and a few drops of potassium-ferrocyanide solution as before. The columns are then compared by standing the cylinder on a white tile and looking vertically down through the liquids. If they are of the same tint the two liquids contain equal quantities of iron, and hence that in the first is equal to the amount contained in the volume of iron solution placed in the second If the tints are not identical, further experiments must be made with varying quantities of iron solution until the required volume is found

Lime.—The filtrate from the iron and alumina precipitate is concentrated by gently boiling in a beaker on a sand-bath until it occupies about 100 c.c. A little more ammonia is now added, and about 2 grammes of finely powdered ammonium oxalate is gradually stirred in, the beaker being removed from the sand-bath for this purpose. It is then replaced on the sand-bath and allowed to boil gently for a minute, after which it is removed and the precipitate allowed to settle. After about half an hour the clear liquid is carefully decanted on to a hard filter-paper, as much of the precipitate as possible being left in the beaker. About 25 c.c. of hot distilled water are now poured into the beaker and the precipitate well stirred, and when it has settled the liquid decanted as before on to the filter. This is continued until the washings no longer give any turbidity with silver nitrate acidified with nitric acid. The precipitate is now washed on to the filter-paper with a stream of hot distilled water and dried in the water-oven. When dry, the filter-paper and precipitate are carefully incinerated in a weighed platinum crucible. There are three methods of treating the precipitate.

1. *As Calcium Carbonate.*—When the weight of the precipitate exceeds half a gramme this will be the best method to employ. The crucible is ignited at a dull red heat till the oxalate has been converted into carbonate. As in all probability some of the carbonate will have been over-ignited and thereby changed to lime, a little finely powdered carbonate of ammonium is now added

to the crucible and gentle heat applied till the excess is completely driven off. The crucible is then cooled and weighed, and the treatment with ammonium carbonate repeated till the weight is constant.

2. *As Lime*.—When the weight of the precipitate is small, ignition to the oxide is the better method. The crucible is heated as strongly as possible with a blowpipe flame for about ten minutes, cooled in a desiccator and weighed. It is then heated again for a further ten minutes and weighed, the process being continued until there is no further loss in weight.

3. *Estimation of Lime by Means of Standard Permanganate*.—When the precipitated oxalate has been transferred to the filter-paper in the manner described above, it may be more rapidly estimated by decomposing it with sulphuric acid and titrating the liberated oxalic acid with potassium permanganate. The equation is

$$5\,H_2C_2O_4+K_2Mn_2O_8+3H_2SO_4=K_2SO_4+2MnSO_4+8H_2O+10CO_2.$$

If this method be adopted the filter-paper is perforated by means of a glass rod drawn out to a fine point and the whole of the precipitate washed through into a beaker with a stream of hot distilled water. A few cubic centimetres of dilute sulphuric acid are next added to liberate the oxalic acid. The temperature of the solution is now raised to about 60° C., and standard permanganate solution is run in from a burette until a permanent pink colour is obtained. Each cubic centimetre of permanganate solution being equivalent to 0·045 gramme of oxalic acid, the quantity of calcium or lime present in the beaker can be calculated.

Magnesium.—The filtrate from the calcium oxalate precipitate is evaporated to dryness in a platinum dish on a water-bath, the last traces of water being expelled by carefully heating in an air-bath at a temperature of about 120° C. The dish is now covered with a clock glass to prevent loss by spirting, and is gently heated over a flame until all the ammonium salts have been expelled. The residue is dissolved in dilute hydrochloric acid, and, if necessary, filtered. To the clear solution a moderate excess of ammonia and sodium phosphate is added, the ammonia being necessary since the precipitated phosphate is slightly soluble in water but not in ammonia solution. The liquid is stirred briskly with a glass rod, taking care not to rub the sides of the beaker, covered with a clock glass and allowed to stand overnight. This delay may be dispensed with if the precipitation be carried out in a stoppered bottle and the mixture thoroughly shaken for about a quarter of an hour. When the precipitation is complete, the clear liquid is decanted through a filter-paper and the precipitate washed by decantation with 1 3 ammonia water. The washing is continued until the filtrate, when acidified with nitric acid, gives no precipitate with silver nitrate. The precipitate is now transferred to a filter and dried. When dry, it is detached as completely as possible from the filter and transferred to a weighed platinum crucible, the paper being separately burnt and added thereto.

The crucible is now ignited for about twenty minutes to convert the magnesium-ammonium phosphate (NH_4MgPO_4, $6H_2O$) into pyrophosphate ($Mg_2P_2O_7$), the weight of which multiplied by 0·3604 gives the quantity of magnesia (MgO) in the precipitate. The total volume of the washings is measured and 1 mgm. added to the weight of the precipitate for each 50 c.c. This is necessary, since the magnesium phosphate is slightly soluble in the ammonia water used.

Alkalis.—A litre of water is concentrated to about 100 c.c. The sulphates are then precipitated by means of barium-chloride solution and filtered off. The filtrate is boiled with milk of lime to precipitate iron and magnesium. These are filtered off, and the barium and calcium in the filtrate are now removed by

the addition of ammonia, ammonium carbonate, and a little ammonium oxalate. Having ensured the complete precipitation of these metals, filter, make faintly acid with HCl, and evaporate the filtrate to dryness in a weighed platinum dish. Now gently ignite it until all the ammonium salts are expelled, then weigh the residue, which will consist of the chlorides of sodium and potassium, removing the last traces of water and free acid by gentle ignition.

If it be necessary to estimate the sodium and potassium separately, dissolve the residue in a little distilled water and evaporate to dryness again on the water-bath and then gently ignite to expel the last traces of acid. Now take up again with distilled water, and by means of standard silver-nitrate solution find the weight of chlorine contained in the mixed chlorides. From these data the alkalis may be calculated. The following example from Whiteley's *Chemical Calculations* will make the method plain :—

The mixed chlorides weighed 1·449 grammes and the chlorine content found by titration was 0·7739. If the whole of the chlorine found had been present as KCl, there would have been 1·6241 grammes of chloride. The difference between this weight and the weight actually found is 0·1751 grammes. Now

The difference between the molecular weights of KC and NaCl	:	the deficiency in weight found	: .	the molecular weight of NaCl	:	x;

where x=the NaCl present in the mixed chlorides.

$$\therefore \quad 16 \;.\; 0{\cdot}1751 :: 58{\cdot}5 \quad x,$$

i e.

$$x = 0{\cdot}6402$$

=weight of NaCl in the mixed chlorides.

The potash may also be determined by converting the residue into the double chloride, $PtCl_4 2KCl$ The residue is dissolved in a few cubic centimetres of water and excess of platinum chloride is added. The solution is evaporated on the water-bath till nearly dry, and alcohol is then added to dissolve out the excess of platinum chloride and the sodium compound. The insoluble potassium salt may be readily washed with alcohol by decantation till the washings are quite colourless, after which it is washed into a weighed dish or filter-paper, dried and weighed After weighing, the precipitate is ignited and the residue of metallic platinum weighed, and from these data the weight of the potash present can be calculated. The sodium is obtained by difference.

Sulphates —Two hundred c c of the water are filtered and acidified with dilute hydrochloric acid and brought to the boil in a beaker Sufficient barium chloride is added to precipitate the sulphates and the contents of the beaker boiled gently for about five minutes on a sand-bath in order to render the fine precipitate easier to filter. The precipitated barium sulphate is allowed to settle and the clear supernatant liquid carefully decanted on to a hard filter-paper. The precipitate is washed as completely as possible by decantation with distilled water and is finally transferred to the filter with a fine jet of hot water. It is then dried and ignited and weighed in the usual way. The weight of the precipitate multiplied by 0·3433 gives the quantity of SO_3 present.

Carbon Dioxide.—The quantity of combined carbon dioxide as CO_2 may be calculated from the temporary hardness, as determined by Hehner's method from the equation

$$MCO_3 + H_2SO_4 = MSO_4 + H_2O + CO_2.$$

Thus 44 parts of CO_2 are equal to 98 of sulphuric acid, or to 100 parts of temporary hardness expressed as calcium carbonate, hence every part of temporary hardness found will correspond to 0·44 part of CO_2

Statement of Results.—We have now arrived at a knowledge of the quantities of the various inorganic constituents of the water, but as yet we know nothing as to the actual form of the combination of the acids and bases These may, however, be calculated from the data at our disposal if we remember the relative affinities of the acids and bases with which we are dealing.

The method adopted is best explained by a concrete example.

A water gave the following result upon analysis :—

Chlorine	5 25	parts per 100,000.
Calcium	25 17	
Magnesium	3 15	
Sodium	2 00	
Sulphuric acid (SO_4)	9 30	
Carbonic acid (CO_2)	37 95	

First we assume that sodium will be in combination with chlorine. Now 2 parts of sodium will combine with $\frac{35{\cdot}5\times 2}{23}$, *i e* 3 08 parts of chlorine, giving rise to 5·08 parts of sodium chloride There are 5·25—3·08, *i e* 2·17 parts of chlorine left over, and these will next combine with magnesium Now 2 17 parts of chlorine will combine with $\frac{24\times 2{\cdot}17}{71}$, *i e.* 0 74 of magnesium, giving 2·91 parts of magnesium chloride.

We next take the sulphuric acid, which will combine with the calcium, and any excess that remains with magnesium Now 9 30 parts of SO_4 will combine with $\frac{40\times 9{\cdot}30}{96}$, *i e* 3 87 parts of calcium, giving 13·17 parts of calcium sulphate We have left 21·3 parts of calcium which will be in combination with carbonic acid, and will require $\frac{21{\cdot}3\times 60}{40}$, *i e* 31·95 parts, giving 53·25 parts of calcium carbonate There are now left 2 41 parts of magnesium and 6·00 parts of carbonic acid (CO_2) which will combine, giving 8·4 parts of magnesium carbonate. Thus we now have the following results —

Sodium chloride	5 08
Magnesium chloride	2 91
Calcium sulphate	13 17
Calcium carbonate .	53 25
Magnesium carbonate	8·40

CHAPTER XIII.

THE PHYSICAL AND CHEMICAL PROPERTIES OF COTTON YARNS AND FABRICS.

BLEACHING is accompanied by a loss of weight, owing to the removal of impurities It alters also the physical constants, such as length, tensile strength, and, in the case of yarns, count and twist Careless bleaching may change the chemical nature of the cotton or fail to remove the impurities Claims for short weight, loss of length, or other faults are not uncommon, and a knowledge of the methods used in determining the constants is essential for every bleacher The more important of these are (1) moisture, (2) count, (3) tensile strength and elasticity, (4) twist of yarns

The Determination of Moisture.—Ignorance of the percentage of water present in yarn or other goods received for bleaching, and in the same goods when finished, often leads to mistaken claims for short weight, as will be shown *later* *The water content of textile materials and its determination is therefore* a matter of much importance The amount of moisture present in a textile fibre is not a fixed quantity even for the same fibre. It varies from day to day and even from hour to hour The weight of the fibre at any particular time depends upon a number of factors, viz —

1 The nature of the fibre
2. The length of time it has been exposed to the air.
3 The temperature of the air.
4 The pressure of the air
5 The quantity of moisture present in the air.

Of these the first, namely, the nature of the fibre, is the only constant factor. All the others are variable. It is obvious that the water content must be variable also Of the variable factors, 3, 4, and 5 are the most important, since they determine what is known as the "relative humidity" of the atmosphere. In short, the amount of water present in a textile fibre depends chiefly upon (1) the nature of the fibre and (2) the humidity of the atmosphere. Thus, if one pound of cotton be weighed on a dry day, and again on another when the atmosphere is loaded with moisture, it will weigh perhaps one ounce more. As the air drys this extra weight will be gradually lost again. When a dry yarn is exposed to a damp atmosphere it takes up water, increasing in weight till an equilibrium is established between it and the air. Similarly a damp yarn exposed to a dry atmosphere gives up water to the air, till the point of equilibrium is reached. When buying cotton or delivering bleached goods by weight it is important to know how much water is included. Without this knowledge claims for short weight cannot be established. But since the water present is a variable

quantity, it is necessary to have some accepted standard. This, in the case of cotton, is 7·834 per cent. That is, cotton which is neither dry nor damp contains 7·834 per cent of water and 92·166 per cent. of cotton When this is the case the cotton is said to be at "condition," and the process of determining the percentage of water present and calculating the weight of cotton present, after allowing for the agreed quantity of water, is termed "conditioning" The name arises from the practice of exposing cotton after spinning to a damp atmosphere in order to allow it to take up moisture and "set." A yarn may be over-conditioned, *i.e.* contain more water than is natural or necessary, or it may be under-conditioned, when it contains less than the standard allowance.

The standard allowance has been determined as follows :—

If clean, dry cotton, protected from dust, be exposed to air and weighed at intervals, it is found that, under average atmospheric conditions, it will absorb 8½ per cent. of its weight of water. This figure is termed "regain" It means that if 100 parts of dry cotton are exposed to air they will absorb 8½ parts of water, the final weight being 108½. The cotton is then said to be in "correct condition" It is not right to say that cotton at correct condition contains 8½ per cent. of water. It does not. The actual percentage of water present is $\frac{8\frac{1}{2}\times 100}{108\frac{1}{2}}$, *i.e.* 7·834. Cotton at correct condition, therefore, contains water 7·834, cotton 92·166. In order to determine the "condition" of cotton we find the percentage of dry cotton present Then we take 8½ per cent. of this dry weight as the standard allowance for water. The sum of these two, termed "correct condition weight," should be 100. If it be more than 100, the cotton is over-conditioned or damp, the excess of water being measured by the difference between the correct condition weight and 100 If, on the contrary, the correct condition weight be more than 100, then the cotton contained less than the standard allowance of water If we buy by weight, and pay upon ascertained correct condition weight, we shall always get proper weight of cotton, however much or little water may be present

The regains are not the same for different fibres. The more important are—

Cotton	8½ per cent
Silk	11 „
Wool and waste	16 „
Worsted and tops	18½ „
Tops with oil	19 „
Noils	14 „
Noils (scoured)	16 „
Flax	12 „

It must be remembered that the terms "dry" and "damp," as applied to air, are only relative. The dampness of the air, or its relative humidity, depends upon the temperature and the actual quantity of water-vapour present. The quantity of water which air can take up is limited by the condition that the pressure of its vapour, independently of that of the air, cannot exceed a certain amount for any given temperature. This maximum pressure is the same as that which the water-vapour would exert if no air were present. The actual pressure of air saturated with water-vapour is the sum of these two pressures, *i.e.* pressure of the atmosphere and maximum pressure of water-vapour at the atmospheric temperature. The maximum pressure exerted by water-vapour at different temperatures has been measured and tabulated. But air is not always,

in fact rarely, saturated with water-vapour. Life would be very unpleasant if it were. But, if not saturated, the water-vapour does not exert its maximum pressure, but only a fraction of it depending upon the percentage of saturation

If we know, or determine by experiment, the pressure exerted by the water-vapour actually present, and find from the table (p. 240) the maximum pressure for water-vapour at the same temperature, then, since the quantities of water-vapour are proportional to these pressures, we have—

$$\frac{\text{Actual pressure of water-vapour}}{\text{Maximum pressure at same temperature}} = \text{fraction of saturation,}$$

or

$$\frac{p}{p_t} \times 100 = \text{percentage saturation or relative humidity,}$$

where

p=actual pressure of the water-vapour

and

p_t=maximum pressure at the same temperature.

The dampness or dryness of air is determined by its relative humidity, and not by the actual amount of water-vapour it contains. If cotton or other textile fibre be exposed to air for a sufficient length of time to allow equilibrium to be established, the percentage of water present is determined by the relative humidity of the air and the temperature.

Determination of Relative Humidity.—If air containing water-vapour be cooled, at constant atmospheric pressure, both air and water-vapour contract. Since the quantity of water-vapour, and its pressure, remain unchanged, a temperature will ultimately be reached at which the water-vapour will saturate the air and exert, therefore, its maximum pressure If the air be cooled below this point, some of the water-vapour is condensed as water or dew. The temperature at which this occurs is known as the dewpoint, *i. e.* the temperature at which the quantity of water-vapour present in any volume of air is just sufficient to saturate it. During the experiment, neither the quantity of water-vapour nor the pressure have been changed, but only the temperature. The quantity of water-vapour present at the dewpoint is proportional to the maximum pressure exerted at this temperature. That is, the water-vapour originally present is also proportional to the maximum pressure at the dewpoint. If the air had been saturated with water-vapour, the original temperature and the dewpoint would have been the same. The quantity of water-vapour necessary to saturate the air at the original temperature is proportional to the maximum pressure for this particular temperature. These maximum pressures can be obtained from the tables. If, therefore, we can determine the dewpoint, we can calculate the percentage humidity from the formula

$$\frac{\text{Maximum pressure at dewpoint}}{\text{Maximum pressure at temperature of air}} \times 100 = \text{percentage humidity.}$$

The following table gives the maximum pressure exerted by the water-vapour at different temperatures :—

Tension of Aqueous Vapour in Millimetres of Mercury from 0° to 35° C.

°C.	mm	°C	mm	°C	mm	°C.	mm.	°C	mm.
0 0	4 600	6 0	6 998	12 0	10 457	18 0	15 357	24 0	22 184
1	633	1	7 047	1	526	1	454	1	·319
2	667	2	095	2	·596	2	552	2	453
3	700	3	144	3	665	3	650	3	588
4	733	4	193	4	734	·4	747	4	·723
0 5	767	6 5	242	12 5	·804	18 5	845	24 5	858
6	801	6	292	6	875	·6	945	6	·996
7	836	7	342	7	947	7	16 045	7	23 135
8	871	8	392	8	11 019	·8	145	8	·273
·9	905	9	442	9	090	9	246	9	411
1 0	940	7 0	492	13 0	162	19 0	346	25 0	·550
1	975	·1	544	1	235	·1	449	1	·692
2	5 011	2	595	2	309	2	552	2	·834
3	047	3	·647	3	383	3	655	·3	976
4	082	4	699	4	456	4	758	4	24 119
1 5	118	7 5	751	13 5	530	19 5	861	25 5	261
6	155	6	804	6	605	·6	967	6	406
7	·191	7	857	7	·681	·7	17 073	7	·552
8	228	·8	910	8	757	8	179	8	·697
·9	265	9	964	9	832	9	285	·9	·842
2 0	302	8 0	8 017	14 0	908	20 0	391	26 0	·988
1	340	1	072	1	986	1	500	1	25 138
2	378	2	126	2	12 064	2	608	2	·288
3	416	3	181	3	142	3	717	3	·438
4	454	4	236	4	220	4	826	4	588
2 5	·491	8 5	291	14 5	298	20 5	935	26 5	738
6	·530	6	347	·6	378	6	18 047	6	·891
7	569	7	404	7	458	7	159	7	26 045
8	608	8	461	8	538	·8	271	8	198
9	647	9	517	9	619	9	383	9	351
3 0	687	9 0	574	15 0	699	21 0	495	27 0	505
1	727	1	632	1	·781	1	610	1	·663
2	767	2	690	2	864	2	724	2	820
3	807	3	748	3	947	3	839	·3	978
4	848	4	807	4	13 029	4	954	4	27 136
3 5	890	9 5	865	15 5	112	21 5	19 069	27 5	294
6	930	6	925	6	197	6	187	6	455
7	972	7	985	7	281	7	305	7	617
9 8	6 014	8	9 045	8	366	8	423	8	778
9	056	9	105	9	·451	9	·541	9	939
4 0	·097	10 0	165	16 0	536	22 0	659	28 0	28 101
1	140	1	227	1	·623	1	·780	1	267
2	183	2	288	2	710	2	901	2	433
3	226	3	350	·3	·797	3	20 022	3	599
4	270	4	412	4	885	4	143	4	·765
4 5	313	10 5	474	16 5	·972	22 5	265	28 5	931
6	357	6	537	6	14 062	6	389	6	29 101
7	401	7	601	7	·151	7	514	7	271
8	445	8	665	8	·241	8	639	8	441
9	490	9	728	9	331	9	763	9	·612
5 0	534	11 0	792	17 0	·421	23 0	·888	29 0	·782
1	580	1	857	1	513	1	21 016	1	956
2	625	2	·923	2	605	2	144	2	30 131
3	·671	3	989	3	697	3	·272	3	·305
4	717	4	10 054	·4	790	4	·400	4	·479
5 5	763	11 5	120	17 5	882	23 5	528	29 5	654
6	810	6	187	6	977	6	·659	6	833
7	857	7	255	7	15 072	·7	790	7	31 011
8	904	8	322	8	167	8	·921	·8	·190
·9	·951	9	·389	9	262	·9	22 053	·9	·369

Tension of Aqueous Vapour in Millimetres of Mercury from 0° to 35° C. (continued).

° C.	mm.	° C.	mm	° C.	mm.	° C.	mm	° C.	mm.
30 0	31 548	31·0	33 405	32 0	35 359	33 0	37 410	34 0	39 565
1	·729	1	596	1	559	1	621	1	786
·2	911	2	787	2	760	2	832	2	40 007
·3	32 094	·3	980	3	962	3	38 045	·3	230
·4	·278	·4	34 174	4	36 165	4	·258	4	455
30·5	463	31 5	368	32 5	370	33 5	473	34 5	680
·6	650	6	564	6	576	6	·689	6	907
7	837	7	·761	7	783	7	·906	7	41 135
8	33 026	8	959	8	991	8	39 124	8	364
9	215	9	35 159	·9	37 200	9	344	9	595
								35 0	·827

The dewpoint may be determined directly by Dines' hygrometer (fig 82). This instrument consists of a box of thin copper through which a stream of cold water can be passed A piece of thin blackened glass is used for a portion of one of the walls, and behind this is the bulb of a delicate thermometer. Cold water, or ice-cooled water, is run slowly through the box, until the temperature of this and the glass reaches the dewpoint Directly the temperature falls below the dewpoint, a film of moisture is deposited from the air upon the outer surface of the glass. When this film appears the stream of water is stopped and the temperature noted. The temperature at which the film disappears is then observed. The mean of these two temperatures is taken as the dewpoint The dewpoint is, however, more commonly determined by means of the wet and dry bulb thermometer (fig. 83).

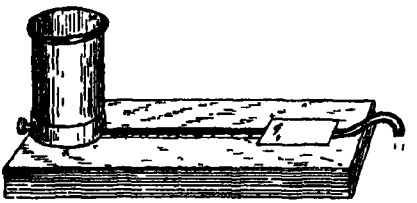


FIG 82.—Dines' hygrometer

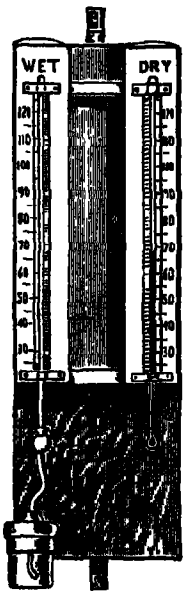


FIG. 83.—Wet and dry bulb thermometer

This consists of two thermometers side by side. The bulb of one is covered with muslin, attached to a wick which dips into a small reservoir containing water. The muslin being wet, the air round the bulb is always saturated with moisture. The temperature indicated by the wet bulb will therefore be lower than that of the air, as indicated by the other, dry bulb, thermometer. The less the relative humidity of the air, the greater will be the difference between the temperatures indicated by the wet and dry bulbs. Conversely, the greater the relative humidity of the air, the more nearly will the readings approximate one another, until finally, when the air is saturated with moisture, both thermometers will indicate the same temperature, *i.e.* the dewpoint.

The dewpoint may be calculated from the formula

$$t - t_{dp} = f(t - t_w),$$

where

t = temperature of dry bulb,
t_w = ,, ,, wet bulb,
t_{dp} = ,, ,, dewpoint;

f is a factor depending upon the temperature of the air, and may be taken from the following table —

f	0	1.	2	3	4	5.	6.	7	8	9.
- 10°	8 76	8 75	8 55	8 26	7 82	7 28	6 62	5 77	4 92	4 04
0°	3 32	2 81	2 54	2 39	2 31	2 26	2 21	2 17	2 13	2 10
10°	2 06	2 02	1 99	1 95	1 92	1 89	1 87	1 85	1 83	1 81
20°	1 79	1 77	1 75	1 74	1 72	1 70	1 69	1 68	1 67	1 66
30°	1 65	1 64	1 63	1 62	1 60	1 60	1 59	1 58	1 57	1 56

Having found the dewpoint, we refer to the table of maximum pressure of aqueous vapour and find those corresponding to the temperature of the atmosphere and the dewpoint. Substituting these in the formula given above, $\frac{p \times 100}{p_t}$, we have the relative or percentage humidity

The formula given above entails a considerable amount of arithmetic For most purposes it is sufficient to regard the temperature of the wet bulb as the dewpoint, and take the maximum pressure at this temperature from the table. Thus:

$$\frac{\text{Maximum pressure at temperature of wet bulb}}{\text{Maximum pressure at temperature of dry bulb}} \times 100 = \text{percentage humidity.}$$

Determination of Moisture.—This, as explained above, is generally termed "conditioning" The process of conditioning is carried out in the following manner —

The net weight of the cotton to be tested is carefully taken Samples are then drawn in such a way as fairly to represent the bulk, from one-half to one pound being necessary for each test Thus, in a bundle of cotton from three to four doles are taken, while in the case of cops or bobbins about two pounds are drawn from different parts of the delivery These samples are divided into three lots and carefully weighed to the nearest quarter dram Two are used for testing, and the third is reserved in case the duplicate tests do not agree. Hank yarn is, of course, weighed directly; but in the case of cop or bobbin yarn the procedure is somewhat different The cops are first weighed. They are then wound into hanks, and the tubes or bobbins, together with any unwound or unwindable residue, again weighed. The difference between the two weights is the weight of the yarn unwound for testing.

These samples are now dried in a specially designed oven at a temperature of 100° to 105° C When all the moisture has been expelled, the residual dry yarn is weighed without removal from the oven, and thus the percentage of dry yarn in the original weight is ascertained, the weight lost being of course the water contained therein. The following are examples —

		lb.	oz	drms.	drms.
1	Weight of original hanks .	1	1	4	= 276
	Weight when dry . .	0	15	6	= 246
	∴ Loss in water	0	1	14	= 30

i.e Percentage dry weight $= \frac{246}{276} \times 100 = 89\ 13$

and percentage of water $= 10\ 87$

2	Weight of cops taken .	1	2	3½	
	Weight of tubes .	0	1	1½	
	Weight of yarn . .	1	1	2	= 274
	Weight when dry	1	0	8	= 264
	Loss in water .	0	0	10	= 10

i e Percentage dry weight $= \frac{264}{274} \times 100 = 96\ 35$

and percentage of water $= 3\ 65$

Having ascertained the percentage of dry weight, we next take 8½ per cent. of it and add it for the regain or allowance of moisture, as has already been explained Thus in Example 1 we have 89·13 per cent of dry cotton The allowance or regain is therefore $\frac{89{\cdot}13 \times 8\frac{1}{2}}{100}$ or 7·57. The sum of these is 89·13+7·57, i e 96 70. This number represents the percentage of true yarn containing the correct percentage of moisture or percentage condition weight present in the sample The difference between this number and 100, viz 3 30, is due to excess of moisture over and above the standard allowances

In Example 2 given above the result is somewhat different Here the percentage dry weight is 96·35 The regain is $\frac{96{\cdot}35 \times 8\frac{1}{2}}{100}$, i e 8·19, and the percentage condition weight is 96·35+8·19, i e 104·54, or greater than 100 This indicates that the yarn is drier than necessary and the excess above 100, i e. 4·54 represents the excess of yarn, containing the proper amount of water present in the sample

Although the test is a simple one, difficulties have to be overcome which necessitate the employment of special apparatus and conditions of experiment The sample to be tested must be sufficiently large fairly to represent the bulk, and for this purpose from one to three pounds is generally required In order to dry so large a quantity, a specially designed oven is necessary, in which the dry cotton can be weighed at the temperature at which it is dried and without removal from the oven. It would be impossible to remove and weigh it outside, since it would attract moisture from the air so rapidly as to make the results practically useless. Finally, a constant temperature must be selected and maintained The most suitable temperature is from 100° to 105° C., since between these limits all the natural water is driven off without any danger of decomposition. If cotton be dried at a lower temperature, it will lose a definite amount of water, but will still retain a portion which it only parts with at a higher temperature. In fact, a portion of the water seems to be more intimately combined with the fibre than the remainder, just as in inorganic crystalline salts a portion of the water of crystallisation is often more firmly combined than the rest.

The drying oven used for conditioning is cylindrical in shape, and consists of four circular casings, between which the hot air circulates before passing out of the escape pipe, the heat being evenly distributed and a uniform temperature

secured. Two of the casings are removable for cleaning purposes. The standard type (fig. 84) is heated by electricity, but may be also adapted to either gas, oil, or steam. The oven is provided with a movable semicircular lid or cover, the other half being permanently closed. Fixed to this is a balance weighing to half a grain, in such a position that one end of the beam is exactly over the centre of the oven. From this end is suspended a movable cage or basket of copper or zinc wire, in which the cotton is placed, and which reaches to the centre of the oven, the suspending rod passing through a hole in the lid. A scale pan is attached to the other end of the beam Near the pillar is an aperture through which passes a thermometer The test is made as follows: The sample is placed in the basket, the lid of the oven replaced, and the sample carefully weighed The gas is then lighted and the temperature of the oven maintained at 100° to 105° C. till the cotton is dry As the moisture is expelled weights are taken from the scale pan until no further loss can be observed. The weight now left in the pan is that of the dry cotton, the weights removed being the amount of water contained in the sample tested The percentage dry weight is now calculated, and from this, as explained, the percentage condition weight is obtained. If the net weight of cotton in the bulk from which the sample was drawn be known, this, multiplied by the percentage condition weight, will give the weight of true cotton, containing the standard amount of water that is present. The following examples will illustrate the method :—

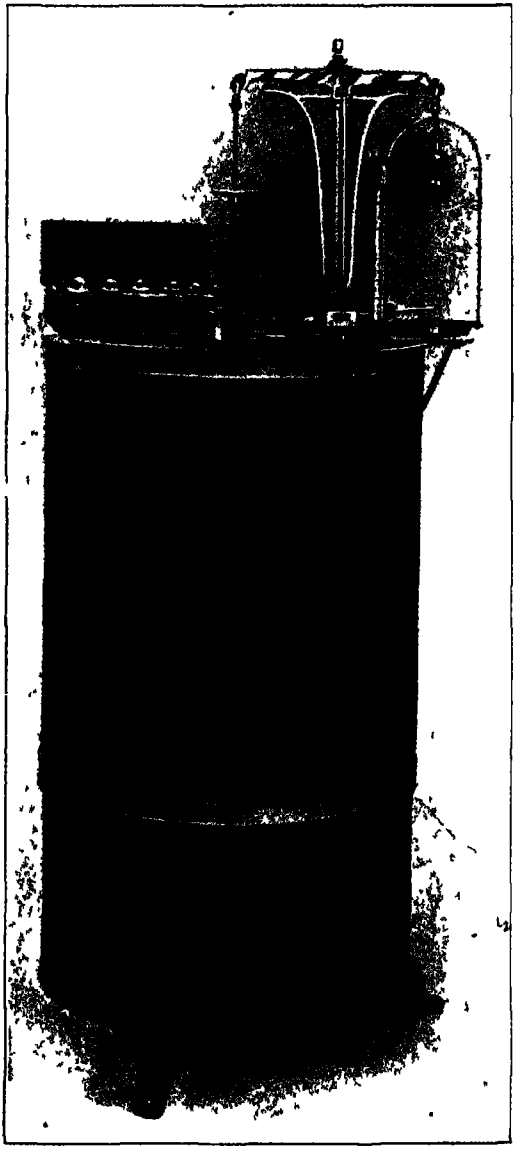


FIG. 84.—Cotton-testing oven.

Example 1.

A bundle of cotton weighed, when tested, 10 19 lbs.
13 ozs. 2 drms. were dried, and, when absolutely dry, weighed 11 ozs. 13 drms. Thus we have—

Weight of cotton before drying, 210 drms. Weight of cotton after drying, 189 drms.

Therefore 100 parts contain $\frac{189}{210}\times 100$ of dry cotton, *i.e.* 90 00

i.e. Percentage dry weight	90·00
Add 8½ per cent regain, *i.e.* $\frac{90\times 8\frac{1}{2}}{100}$	7·65
The sum of these is the condition weight, *i.e.* percentage .	97 65
Therefore loss or excess moisture	2 35

Therefore the bundle contained $\frac{10\ 19\times 97\ 65\ \text{lbs}}{100}$ of true yarn at correct condition, *i.e.* 9 95 lbs.
But it should have contained 10 lbs., hence the shortage is 0 05 lb or 0¾ oz

Example 2.

Weight of bundle when tested . .	10 17 lbs.			
Weight taken for testing, *Exp* 1,	11 ozs. 5½ drms.	*Exp.* 2,	11 ozs. 4½ drms.	
„ when dry,	10 „ 7½ „		10 „ 6½ „	
Hence percentage dry weight	92 28		92 24	
Mean percentage dry weight .	92 26			
Add regain 8½ per cent . .	7 84			
Percentage condition weight	100 10			

$\therefore$ Condition weight of the bundle $=\frac{10\ 17\times 100\ 10}{100}=10\ 18$ lbs.

The process is just the same for fibres other than cotton, but the regain is different The following examples illustrate the method for worsted and silk —

Example 1.

1 lb of worsted yarn weighed, when dry, 13 ozs 8 drms , *i e* 216 drms

Percentage dry weight $=\frac{216}{256}\times 100$	84 38
Regain 18¼ per cent $=\frac{84\ 38\times 18\ 25}{100}$.	15 40
. Percentage condition weight	99 78

Example 2.

200 drms of silk weighed, when dry, 180 drms.

Percentage dry weight $=\frac{180}{200}\times 100$	90 00
Regain 11 per cent. $=\frac{90\ 00\times 11}{100}$	9·90
$\therefore$ Percentage condition weight	99 90

In the case of mixed yarns we must, first of all, know or estimate the proportion of each fibre present. The regain is then calculated from these proportions.

Example

A yarn contains per 100 parts of dry weights: cotton 40, silk 10, wool 50 Find the regain

The cotton contributes	$\frac{40 \times 8\,5}{100}$ . .	3 400
The silk „	$\frac{10 \times 11}{100}$	1 100
The wool „	$\frac{50 \times 18\,25}{100}$.	9·126
The regain is the sum of these, *i e*		13 626

Count and its Determination.—Yarns are spun so that there is always a fixed relation between the length obtained from a given weight of fibre. Thus, there is definite relation, in all yarns, between weight and length. This relation is known as the "count," "size or number" of the yarn. The count of a yarn is determined by measuring, carefully, any given length and weighing it. From the results, the relation between the two, *i.e.* the count, is calculated, *e g* the number of yards to one pound of the weight of 1000 yards in drams. There are, unfortunately, many systems or different units of measurement. No one system is universal even for the same fibre, nor can one be translated readily into others Moreover, *in some systems the weight is fixed and the length* variable, while in others the conditions are reversed In the first case, the count is measured by the length necessary to make up a given weight, such as the number of yards to a pound or ounce In the second, the count is the weight of a fixed length, *e g.* the weight of 1000 yards in drams The existence of so many systems is due to the fact that the textile industries were originally localised, and, owing to the lack of means of intercommunication, trade was restricted to narrow limits. Expanding trade and foreign competition makes the adoption of a simple universal method very desirable The chief difficulty to be overcome is the use of the metric system This was recommended by a conference of experts in Paris in 1900, and is known as the "International System" It is based upon a fixed weight and variable length, the unit being 1 gramme and 1 metre respectively If 1 metre of any yarn weighs 1 gramme, it is said to be No. 1, if 20 metres, No 20; if X metres, No. X. Yarns are sometimes folded or doubled, *i e* two or three single threads are twisted together, making a yarn two or three times as coarse as the original threads. Under the metric system the yarn number or count indicates the final thread, however many strands it contains. Thus, if the yarn is composed of three threads, and 20 metres weigh 1 gramme, the count is 20 threefold, or 20/3, whatever the counts of the separate threads may be.

The principal systems of counts will now be described

Cotton count, for cotton yarn and spun silk. A hank of cotton is 840 yards. The number of hanks contained in 1 lb. is the count. In the case of folded yarns the count indicates the original thread before folding. Thus twofold 40 or 40/2 means single 40 doubled to make 20

Worsted Count.—A hank of worsted yarn is 560 yards. The number of hanks to the pound is the count. 2/40 means single 40 doubled to 20. It should be noted that while twofold cotton is written 40/2, in the case of worsted the order is reversed, viz 2/40

Yorkshire Count.—This is based upon a hank of 256 yards, the count being the number of hanks to the pound.

Linen, Hemp, and Ramie Count.—The hank is 300 yards. The count is the number of hanks to the pound.

In all these systems we have a constant weight and variable length. In the following the length is constant and the weight variable.—

Raw Silk Count.—The hank or skein contains 450 metres. The weight of this skein in half decigrammes (*i.e* 0·05 gramme) is its count.

Raw Silk Denier Count.—The skein is 476 metres. The weight of this skein in deniers is its count A denier is 0·0532 gramme.

Manchester count for raw or thrown silk. The weight in drams of 1000 yards is the count.

Measurement of Count.—To determine the count of a yarn a suitable length is measured off, avoiding either strain or slackness, and carefully weighed. From this weight the required count is calculated The length taken depends upon the fineness of the yarn. For cotton and worsted 120 yards, termed a lea, is convenient, but for raw silk, or even very fine cotton yarn, a greater length must be taken.

The method may be illustrated by a few examples.

Cotton.—A lea of cotton (or 120 yards) is 1/7 of a hank. A pound contains 7000 grains No 1 cotton (*i e* one hank to the pound) means that 840 yards weighs 7000 grains. Therefore 120 yards would weigh 1000 grains Hence, if we measure off 120 yards of a cotton yarn, weigh it in grains, and divide 1000 by this weight, we shall obtain the count of the yarn.

Example 1.

120 yards of single cotton weigh 17 25 grains

$$\text{The count is } \frac{1000}{17\ 25}, \text{ i e. } 57\ 97/1.$$

Example 2.

120 yards of twofold cotton weigh 40 grains.

$$\text{The count is } \frac{1000}{40}, \text{ i e. } 25.$$

Since the yarn contains two threads, it is made from two single 50's doubled together to make a thread twice as coarse, *i e* 25's. The count is written 50/2.

Wool.—Eighty yards is 1/7 of a hank of 560 yards If we measure 80 yards and weigh it in grains, the count can be obtained, as with cotton, by dividing this weight into 1000. The machine which we use for measuring gives the best results with 120 yards, *i e* with 3/14 of a hank. For No. 1 the weight of this length is $3/14 \times 7000$ grain, *i.e* 1500. Hence we can get the count by dividing 1500 by the weight in grains of 120 yards.

Example.

120 yards of single worsted yarn weigh 30 grains.

$$\text{The count is } \frac{1500}{30}, \text{ i e. } 50 \text{ or } 1/50.$$

Ramie, etc.—The hank is 300 yards, and 120 yards is 2/5 of a hank. For No. 1, 300 yards weigh 7000 grains. Therefore, 120 yards weigh 2/5 of 7000, *i.e.* 2800. Thus to obtain the count we may measure 120 yards, weigh it in grains, and divide this weight into 2800.

Silk.—If we want to express the count in terms of drams per 1000 yards, we may measure off 120 yards and weigh it in grains. Remembering that a dram

contains 16 grains, it is simple to calculate the weight of 1000 yards in drams. When deniers or other counts involving the metric system are required, the calculations are rather difficult In such cases it is better to weigh in grammes.

Example.

120 yards of silk weigh 2 50 grammes Find the count in half decigrammes per 450 metres.

120 yards=120×0 9144 metres=109 73.

$$450 \text{ metres weigh } \frac{2\ 50 \times 450}{109\ 73} \text{ grammes, } i.e.\ 10\ 25$$

$$\therefore \text{ count} = \frac{10\ 25}{0\ 05} = 205$$

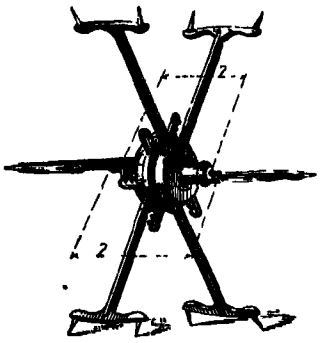


FIG. 85

The count is determined by carefully winding and weighing a measured length of the yarn, sufficient tests being made from different portions of the sample to secure a fair average The length selected is generally one lea, or 120 yards The hank is placed on a light revolving Schwarzenbach wheel (fig 85), and the required length measured on a wrap reel of 54 inches diameter, provided with a recording measuring dial (fig 86) Each complete revolution of the pointer measures 120 yards, and is marked by the automatic ringing of a bell connected with the recorder The apparatus is also provided with a travelling mechanism to prevent overlapping The base of the instrument carries a number of skewers upon which cops or bobbins may be placed, and between these and the reel are a number of glass hooks through which the yarn passes in order that even tension may be maintained. It is of great importance that there should be neither undue tension nor sagging of the yarn, since in either case the measurement will be inaccurate In the revolving wheel illustrated, tension is adjusted by means of a small weight suspended from the axle The necessary length having been measured, it is removed from the reel and carefully weighed on a balance that is delicate to at least one-tenth of a grain, and which is enclosed in a glass case to protect it from currents of air As a rule, ten tests are made from different cops or hanks. As each one is removed from the reel it should be placed in an air-tight or stoppered bottle If left lying about it may lose moisture and thus affect the accuracy of the test When sufficient leas have been measured off, they are carefully weighed and the average weight of a lea determined. From this weight the count can be exactly calculated in the manner shown in the following example Ten leas of a reputed 32/1 were reeled and weighed, the average weight per lea being 34 grains One hank weighs 7×34 grains=238 grains. Since there are 7000 grains in a pound, 1 lb. of the cotton will contain $\frac{7000}{7\times34}$ hanks, *i.e.* 29·41. Since the yarn is single, the count is therefore 29·41/1. If it were doubled, the count would be 58·82/2.

Example.

Ten leas of 70/2 cotton reeled and weighed gave 120 yards=29 5 grains

$$\text{1 lb. contains } \frac{7000}{7\times29\ 5} = \frac{1000}{29\ 5} \text{ hanks} = 33\ 9$$

Thus the cotton would be 33·9 if a single, but since it is doubled the count is 67·8/2.

The weight of a given length of yarn is affected by the amount of water it contains. This varies from day to day unless the temperature and humidity of the atmosphere remain constant. Two persons testing the same yarn at different places may get different results unless allowance be made for difference in the water content of the yarn. For accurate work, or in cases where disputes may arise, the count should be calculated upon the yarn at "correct condition."

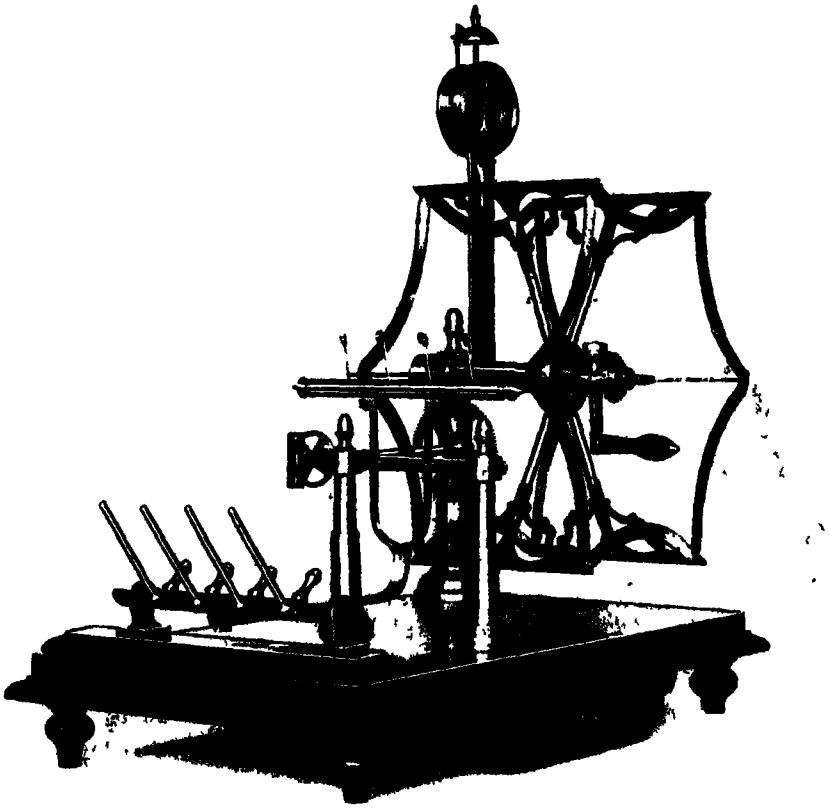


FIG 86.—Hand wrap reel

This is a constant number. However much or little water a yarn may contain, its true count at correct condition is always the same. The "true" or condition count may be obtained from the "apparent" count by dividing the latter by the percentage condition weight of the yarn and multiplying by 100, *e.g.*

Count determined as received . .	32 00
Percentage condition weight . . .	96 50

$$\text{True or condition count} = \frac{32\ 00}{96\ 50} \times 100 = 33\ 19$$

The leas measured off for the test may be used to determine moisture. They are placed together in a weighing bottle and weighed. They are then dried in

an oven and again weighed in the weighing bottle. The dry weight of the leas is thus obtained and the true count can be calculated.

Example.

Ten leas of cotton, as measured, weighed 190 grains. The count of the yarn, as received, was $\frac{1000}{19}$, *i.e.* 52·63.

When dry the weight was 180 grains. The condition weight of these 10 leas is therefore $180+\frac{180\times 8{\cdot}5}{100}$ grains, *i.e.* 195·30.

The true count is therefore $\frac{1000}{19{\cdot}53}$, *i.e.* 51·20.

The true count of a yarn is also affected by weighting matter or excess of oil, if present. In such cases the weighting matter must be estimated and allowed for if the true count is required.

Example.

The apparent count of a cotton yarn is 200. Analysis shows that it contains 5 per cent. of cocoanut oil. What is its *true* count? Since the count is 200 the weight of 120 yards would be 5 grains. Of this 5 per cent. is oil. Hence the weight of cotton in 120 yards would be $\frac{5\ \ 95}{100}$ grains, *i.e.* 4·75.

The true count is $\frac{1000}{4{\cdot}75}$, *i.e.* 210·5.

If we required the *true* count at correct condition, the oil would, first, be extracted by means of ether or a similar solvent, and the residual yarn then dried and weighed. The "regain" would then be calculated and added to the weight of the dry oil-free leas.

Example.

120 yards of cotton were extracted and dried. The weight of the dry extracted yarn was 16 grains. The regain would be $\frac{16\times 8\frac{1}{2}}{100}$ or 1·36. Hence, the weight of the lea at correct condition is 17·36 grains and the "true count" at correct condition is $\frac{1000}{17{\cdot}36}$, *i.e.* 57·6.

In measuring count, care must be taken to make enough tests to get a fair average, and within reasonable limits the greater the length measured the more accurate will be the results. The following table shows the best lengths to measure:

Up to 40's . . .	120 yards.
40's to 80's	240 ,,
80's to 100	480 ,,
Very fine count . . .	1000 ,,

When more than 240 yards are measured, the hank must be weighed before and after reeling, the difference between two weights being the weight of yarn reeled. This is necessary, since the constant revolution of the widely spread yarn on the wrap reel may cause the loss of sufficient water, especially in a dry room, to seriously affect the accuracy of the count. When any considerable length is measured, great care must be taken to prevent overlapping by stopping every now and then and pushing the reeled yarn to one side. Machines can, however, be obtained which will wind up to 1000 yards without overlapping.

Care must be taken to make enough tests from different cops or hanks to get a fair average. At least ten are necessary. When these have been made, each 120 yards should be weighed separately and the count worked out In this way we can form an estimate of the variation in the count. If the whole of the lots measured were weighed together we should only get the average count. This is illustrated by the following example of cotton yarn :—

	Weight of 120 Yards in Grains.	Count.
Test No 1	12 55	78 69
,, ,, 2	12 45	80 32
,, ,, 3	12 70	78 66
,, ,, 4	12 95	77 22
,, ,, 5	12 00	83 33
,, ,, 6	12·35	80 97
,, ,, 7	13 10	76 33
,, ,, 8	12 70	78 66

Mean count 79 27

In a perfect yarn the count would be uniform throughout. In practice it varies from yard to yard, but in a considerable length the variations balance one another approximately. The greater the length reeled for weighing the more constant will the count appear. In expressing counts it is usual to give the average, but in the case of silk the maximum and minimum are given, *e.g.* 62/67.

It is sometimes necessary to know the equivalent counts in two different systems These can generally be obtained from tables, but are readily calculated from the definition of unit of count

Example.

What worsted count is equivalent to 50 cotton ?
1's worsted means 560 yards to 1 lb
1's cotton means 840 yards to 1 lb
Hence, if x be the required worsted count, we have—

$$560 \,.\, 840 \,.:\, 50 \,.\, x$$

$$560\,x = 50 \times 840.$$

$$x = 75.$$

Folded Yarns.—These have been referred to above. Generally they consist of two or more threads, of the same material and count, mechanically twisted together. When this is the case the count of the folded yarn is approximately that of the original yarn divided by the number of threads. The exact count depends of course upon the amount of twist put in during folding. Folded yarns can be made from threads of different counts. The count of the resulting yarn may be calculated upon the following principles —

Example.

What is the count of cotton yarn obtained by folding together 20's and 10's ? If x be required, then—

$$\frac{7000}{x} = \frac{7000}{20} + \frac{7000}{10}; \quad \frac{1}{x} = \frac{1}{20} + \frac{1}{10} \quad \therefore \quad x = 6{\cdot}66.$$

Measurement of Length.—If sufficient tests of counts have been made to ensure a fair average, the length of yarn present in a bundle may be calculated from the count and net weight. Thus, if the count of a bundle is 31·5/2, and the net weight 9 lbs 12 ozs, the length will be $15{\cdot}75 \times 840 \times 9{\cdot}75$ yards If from 240 to 480 yards be reeled off for each test, and twelve tests be made each from a different hank, this method is unimpeachable. Sometimes two or three knots are taken and reeled; but it must be obvious that these cannot give such a fair representation of the bundle as ten or twelve shorter lengths from as many different knots. In reeling long lengths, great care must be taken to prevent undue slackness, tension, or overlapping.

The direct determination of length may be carried out by means of a special machine made on the principle of the wrap reel, but which will take ten hanks at once and measure up at least 1000 yards without overlapping. The ten hanks, having been carefully weighed, are put as evenly as possible upon the holders and wound off. Care must be taken to stop the machine immediately if one of the threads breaks, since the recording arrangement is not thereby thrown out of gear. As each hank is wound the machine is stopped and the length noted. From the sum of the lengths measured and their weight the total length present in the bundle, as well as the count, can be ascertained For the measurement of count this method is of course superior to that depending upon the measurement of leas, since the greater length ensures a better average. The following is an example of the method .—

Ten hanks of cotton weighed 1 93 lbs These measured 3205, 3217, 3220, 3220, 3225, 3300, 3325, 3330, 3355, and 3380 yards

The total length measured was 32,777 yards.

The net weight of the bundle was 9 80 lbs.

Hence the total length was $\frac{32{,}777}{1\ 93} \times 9\ 80$, *i.e.* 166,432 yards, and the count is $\frac{32{,}777}{1\ 93 \times 840}$, *i.e.* 20 22.

Count of Cloth.—This is determined as follows —

1. *Weft Count.*—The cloth is laid upon a plate having a square opening of a definite size, generally 1 inch. The number of threads is then carefully counted with the aid of a lens

2. *Warp Count* —The process is the same as for the weft, but the standard adopted is generally $\frac{15}{16}$ of an inch. Frequently, however, it is the custom to simply measure the number of threads each way in a square having $\frac{1}{4}$ of an inch edge.

TENSILE STRENGTH AND ELASTICITY

A yarn must have sufficient tensile strength and elasticity to stand the strain of the machines used in weaving it into a fabric Yarn used for warp threads, *i.e.* those running longitudinally through the fabric and forming its skeleton, must be stronger than weft threads used to fill up the spaces and running transversely.

The tensile strength of a fibre or thread is expressed as the weight necessary to break a given length with direct and longitudinal tension.

The elasticity is the increase in length at the breaking-point, and is expressed as a percentage. In a fabric the various threads give each other mutual support Thus, a fairly strong fabric may be made from threads which are individually too weak to stand the strain of weaving or manufacture. To enable them to

do this they are "sized," *i e.* treated with some strengthening mixture, such as starch or glue, before weaving. The size may be removed during the finishing processes applied to the fabrics. The various textile fibres have different tensile strength and elasticity. The strength of a yarn or fabric will depend, therefore, in the first place, upon the inherent tensile strength of the fibre from which it is made. There are, however, other factors which have important effects. For the same material the tensile strength of a yarn varies inversely with the count. Thus, No. 1 is twenty times stronger than No 20 if both are made from fibres of the same quality. Other factors are (1) length of fibre, (2) fineness and evenness of diameter, (3) healthiness or maturity, (4) amount and regularity of twist introduced during spinning, (5) humidity of the atmosphere.

Length of Fibre.—Short fibres cannot be twisted together as easily as long ones, and when twisted do not hold together so tenaciously For any given fibre the best yarns are always spun from selected long fibres. Evenness in length is also of importance for the same reason. Long fibres are separated from short ones by such processes as carding and combing.

Fineness and Evenness of Diameter.—The finer a fibre the greater is the amount of twist which can be imparted during spinning. If the diameter be variable, the twist will be uneven Where the fibres are fine there will be more than where they are coarse If we try to put enough twist into the coarse fibres we shall have too much in the finer fibres Too much twist, like too little, is a source of weakness.

Healthiness and Maturity of Fibres.—Cotton grown in a bad, cold, or wet season does not ripen properly, and is consequently deficient in the layers of cellulose which give it its inherent strength As a general rule, when cotton is plentiful and cheap it is stronger than when it is scarce and dear. Similarly, badly nourished or diseased animals produce only a low-grade wool or hair, and unhealthy silkworms a low-grade silk.

Amount and Regularity of Twist.—During spinning the individual fibres are twisted round a longitudinal axis The twist bears a definite relation to the count of the yarn Too little twist allows the fibres to be drawn out easily and the yarn is weak Too much twist tends to cause knots which catch in the machines It also reduces the elasticity Uniformity of twist is also very important This depends, largely, upon evenness in length and diameter of the fibres. In a perfect yarn the twist should be nearly constant from inch to inch. In practice, however, it varies very much, and is only fairly constant over a considerable length. This is seen in the following examples of cotton yarns, the figures being the number of twists per inch.—

Count of Yarn	Twist per Inch Maximum	Twist per Inch Minimum.	Average
50/1	60	10	26
70/1	60	26	42
90/1	41	19	26
100/2	35	21	24
120/2	40	19	27

Humidity of the Atmosphere.—This factor exercises a very important effect upon tensile strength. Its effect is not the same for all fibres. Thus, the tensile strength and elasticity of cotton and flax are increased by increasing the

humidity of the atmosphere to which they are exposed, but with wool the effect is the opposite. Lancashire has become the centre of the cotton-spinning trade largely because of the high percentage humidity of its atmosphere. The following examples show the effect of increasing humidity in the case of fabrics :—

Relative Humidity	Strength of Serge	Strength of Cotton Drill	Strength of Canvas.
44 per cent	186 lbs	521 lbs	599 lbs
82 ,,	160 ,,	592 ,,	729 ,,
Variation	14 per cent.	12 per cent	18 per cent

The effect of moisture upon artificial silks is, in some cases, very marked, tensile strength falling rapidly with increasing humidity. The decrease in the case of wool is not of great moment, because the strain of the machines is not great and the diminished strength of the fibre is still sufficient. With cotton it is different. A yarn which, when dry, is too weak to pass through machines without constant breaking, may be made strong enough to use satisfactorily by increasing the humidity of the atmosphere and giving the yarn time to come to a state of equilibrium. The following tables will show the importance of this point --

Count of Yarn	Humidity	Tensile Strength	
50/1	67	21 6	single threads.
	70	24 7	
	72	26 4	
	76	26 6	
	87	26 8	
50/2	69	40 6	single threads
	73	45 5	
	77	45 5	
40/2	50	90 8	leas
	87	119 6	
32/2	50	108 8	leas.
	80	124 3	
	86	137 8	
100/2	37	67·0	leas
	79	69 5	
	87	70 3	

It follows, from these results, that, for accurate work, and to obtain really comparable results, strength tests should always be made under known or standard conditions of humidity.

Measurement of Tensile Strength of Yarns.—The tensile strength of a yarn is expressed in two ways, viz. (1) in lbs per lea of 120 yards, (2) the weight required to break a single thread The breaking strength per lea is measured in the following manner:—

The cotton is reeled in leas and the two ends carefully knotted together.

The lea is then removed and placed carefully and evenly spread out upon the two hooks of the testing machine shown in fig. 87.

These hooks are capable of being moved vertically in opposite directions by the turning of a screw, and they are connected with a weight and lever and a recording dial which registers the pull of the yarn in lbs. Before any pull is exercised, the cotton stretches owing to its elasticity, and a pointer and scale are attached to the vertical column to register this elasticity. The screw is either turned by power or hand. If by hand, great care should be taken to prevent jerking and to maintain a perfectly uniform rate of turning, otherwise erratic results may be obtained. The upper hook is connected with a chain which passes over a cylinder to which is attached a lever and weight and pointer. Before commencing a test the pointer is set at zero, when the weight hangs vertically. When the screw is turned the tension of the yarn causes the weight to be raised until the yarn breaks, when the weight is arrested by a catch working on a semicircular rack The dial is then read and the machine reset

In order to get regular results the handle must always be turned at the same rate If the speed is greater, the yarn will show a greater breaking strength than when turned slowly. From experiments made by Bowman it was shown that in order that the breaking strength of the yarn, as indicated by the machine, may correspond with the actual breaking strength due to gravity, the hand of the dial should travel round the face in eight seconds For these reasons it is better, if possible, to have the machine worked by power. In the machine shown in fig 87 the power is supplied by means of a motor which actuates a strong square-thread screw which revolves within a steel casing. In another form of machine the lea is stretched between two horizontal hooks, and the weight is replaced by a chain passing over a pulley carrying a vessel into which water can be poured, the weight required to break the lea being afterwards measured or weighed.

The testing of the strength of leas of yarn is open to many objections What one really tests is the breaking strain of the weakest threads in the lea, or those that have the least elasticity. Then, again, the even spreading of the lea on the hooks affects the result, and to a certain extent the tensions under which the lea has been reeled Thus, the difference between consecutive tests is very great. The following illustration serves to show the difficulties attending the testing of leas Suppose that four turns of yarn are actually gripped at the hooks, that they have different elasticities, and that they have the following breaking strains and elongations before breaking :—

A	breaks	at	10	lbs	with	an	elongation	of 1 inch.
B	,,	,,	5	,,	,,	,,	,,	2 inches
C	,,	,,	3	,,	,,	,,	,,	3 ,,
D	,,	,,	4	,,	,,	,,	,,	4 ,,

When A breaks the strain is $10+2\frac{1}{2}+1+1=14\frac{1}{2}$ lbs., and hence the average breaking strength is $14\frac{1}{2} \div 4=3{\cdot}526$, but the average is

$$\frac{10+5+4+3}{4}=5{\cdot}5 \text{ lbs.}$$

If the elasticity be neglected and say twenty turns of yarn, in which there is one weak spot which will withstand the strain of 3 ozs., the remainder being uniform at 6 ozs., be placed on the hooks in the ordinary test, the pull will be 60 ozs., but if there had been more weak spots it would still have been the same.

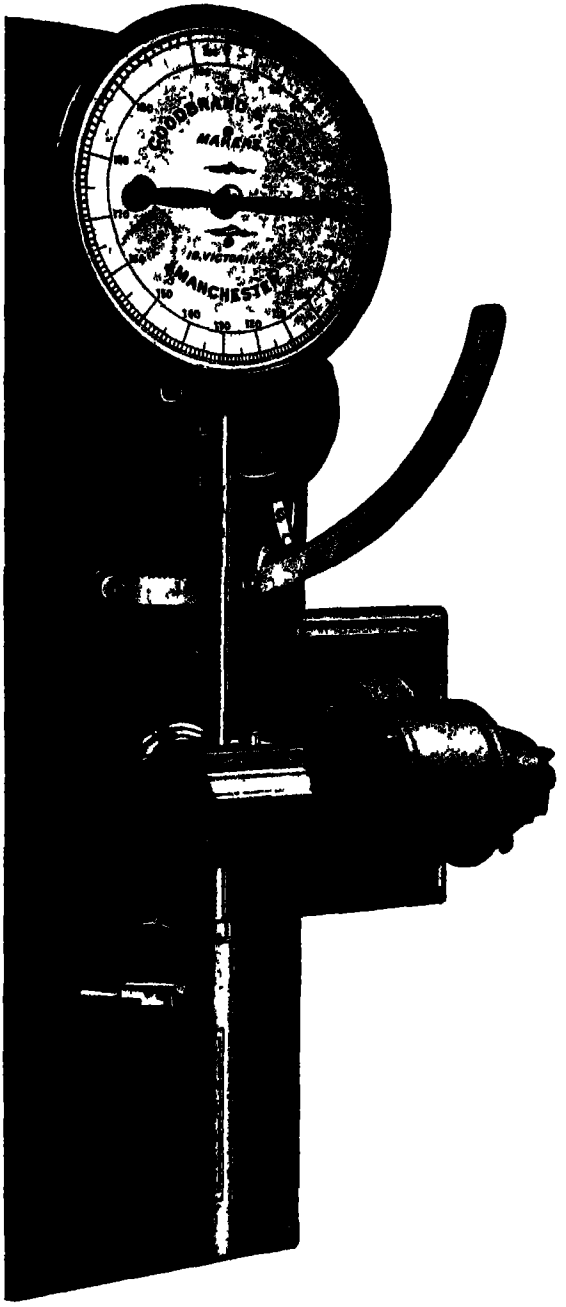


FIG 87.—Yarn-testing machine.

That is to say, both yarns would test the same, although one would be much superior to the other

It is obvious that the only way scientifically to test strength and unevenness is to test the breaking strength of a number of single threads Several machines

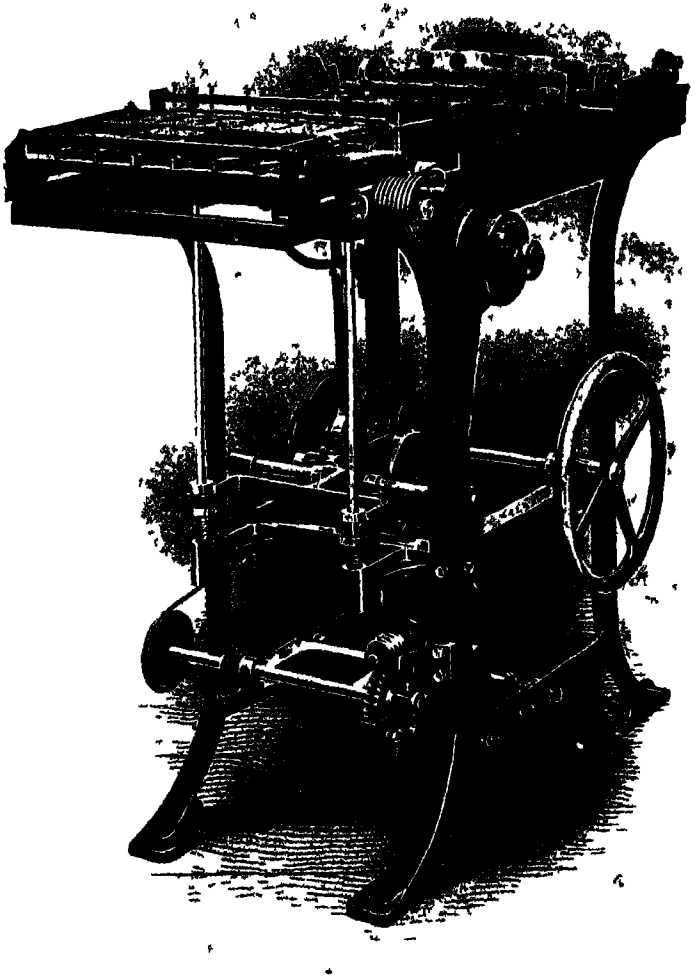


Fig 88 —Cook's single thread tester

are in use for this purpose, but as a rule they only test one thread at a time, thus making the operation a very long one The automatic single thread tester, made by Messrs Cook & Co of Manchester, is capable of making a large number of tests simultaneously and recording their strength on a chart The apparatus is shown in fig 88 From commencement to finish of one test there are four operations—

1. An inward movement of the carriage presenting yarns to the nips at the point of the machine

2. An outward movement allowing a definite length to be delivered, and the breaking of this against specially constructed springs

3 Record of the strength on the diagram paper during the inward movement of the carriage

4 Clearing the tested yarn from the nips ready for the next test

The following details of the working of the apparatus are given in the *Textile Recorder Year Book*, 1924

"The cops or bobbins are placed on skewers mounted upon a frame having a traversing motion Each thread is passed through the tensioning hooks and eyes and between a clip When the machine is started the frame moves forward, and a plate lying underneath the threads rises and lays each thread into the jaws of another series of clips, which immediately close When the frame or carriage has receded about 12 inches, the clips in the carriage close on the threads, and as the carriage continues its outward movement for about another 4 inches, strain is put on the threads The strain distends a series of springs mounted at the rear end of the second set of clips This distension draws a series of pointers along until the several threads are broken, then the pointers are pressed down into the diagram slip, at the positions to which the pointers have been pulled, and thus a record of the breaking load is made The broken ends are cleared away from the clips, the pointers pushed back to zero, and the whole cycle of movements is repeated about eighty times, when the machine is stopped automatically The record of the breaking strength of the several threads is shown on a punctured slip, and the variations are readily observed

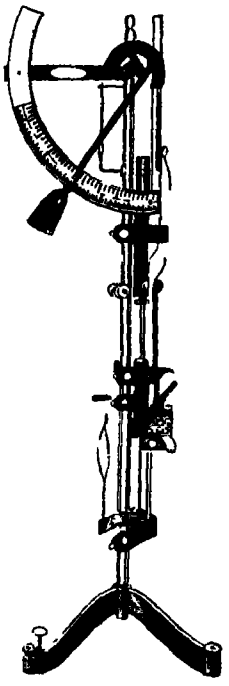


Fig 89 Baer tester

"Different strengths of springs are used for various qualities and counts of yarn

"The only apparently weak part of the machine is the spring, and to eliminate error the greatest possible care is exercised in the selection of the springs"

The Baer Tester (fig. 89) is also suitable for measuring the strength and elasticity of single threads It has an oil-plunger controlled pull and a removeable counterweight The thread is held by two clips and the plunger allowed to fall As this takes place, the weighted arm is raised until it breaks the yarn, when the arm is arrested by a catch, while a pointer shows the breaking strength.

The O'Neill Breaking-load Test for Single Hairs (*J Text Inst*, 1924, T 282) —The modified O'Neill apparatus used is shown in fig 90[1] It consists of a cylinder A, about 50 cm. long and 6 cm wide, containing water which supports a tubular float B, about 1·6 cm. wide The specimen to be tested is mounted by means of sealing-wax across a hole 1 cm. wide in a slip of paper P (fig 91),[1] the ends of which are pinned to the holders K_1 and K_2. The paper is cut along the dotted lines and water run out from the cylinder until the free centimetre length of hair just begins to bear the weight of the float, this state

[1] Illustrations by courtesy of the British Cotton Industry Research Association.

being indicated in fig. 90 Water is now drawn off through the capillary jet J into a measuring vessel until the hair breaks The breaking load on the hair is $V\ r^2/(R^2-r^2)$ grammes weight, where V is the volume of water run in cubic centimetres and r and R are the radii of the float and cylinder respectively in centimetres

Oxley (*J Soc Dyers and Col*, 1923, p 176) has described a new test for yarns, called the oscillating-stress test, which aims at a representation of the variable stresses accompanying certain motions of a loom. Twelve threads, consecutive specimens, are subjected to cyclical stress variations, the stress varying approximately in a simple harmonic fashion An illustration of the apparatus is shown in fig 92 It was found that although the load at no time even approached the normal breaking load, yet the specimens could be broken by a sufficient number of oscillations, this effect being due to the accumulation of a minute permanent set in the yarn at each oscillation The number of oscillations is thus a measure of the capacity of the yarn to withstand this type of variable stress Consecutive specimens of mule yarn were tested in this way, and it was found that although most of the specimens could withstand only a few hundred oscillations, yet those specimens which came from near the spindle tip of the stretch withstood 5000 oscillations without rupture. In these specimens the twist is high, and the permanent set produced by an oscillation is infinitesimal All these methods of testing agree in attributing this type of unevenness of mule yarns to the intermittent character of the mule mechanism.

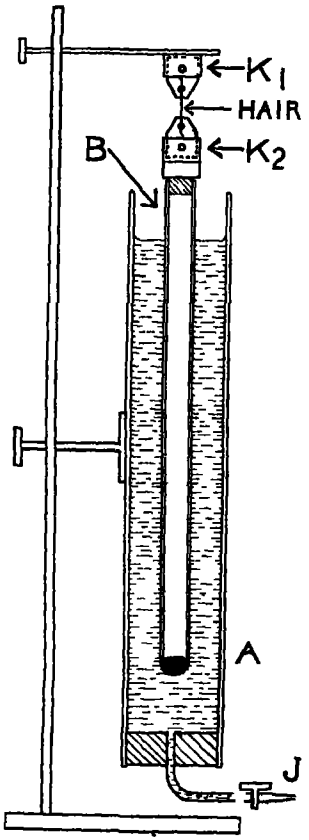


Fig 90

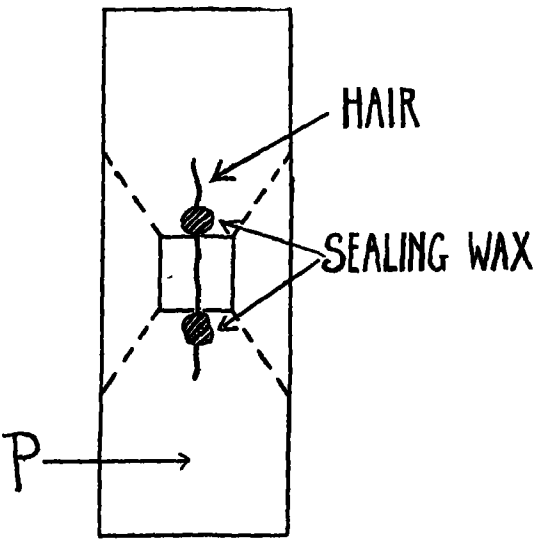


Fig 91

O'Neill breaking-load tester

Testing the Strength of Piece Goods.—In the first place it must be noted

that the habit of testing the strength of a bleached fabric by the hands is quite useless, except in the case of visibly tendered goods The only reliable method is to use some form of mechanical apparatus in which the breaking strength is tested automatically against a spring or dead weight Breaking tests, before and after a process, afford the most certain means of detecting tendering, provided the tests are always carried out under strictly comparable conditions and a sufficient number are made to obtain a fair average A convenient form of apparatus is shown in fig 93, made by Messrs Goodbrand & Co It consists of a dial A, with divisions corresponding to actual weights When the material breaks the pointer remains stationary, thus registering the breaking strain in pounds The pointer is set at zero by releasing the catches A, which set the handle H free, thus allowing the weight J to find its own centre and bring the pointer back to zero A brass plate engraved in inches shows the stretch of the material before it breaks B and B are clamps for fixing the material to be tested They are worked by two eccentric levers, cams C and D, which are

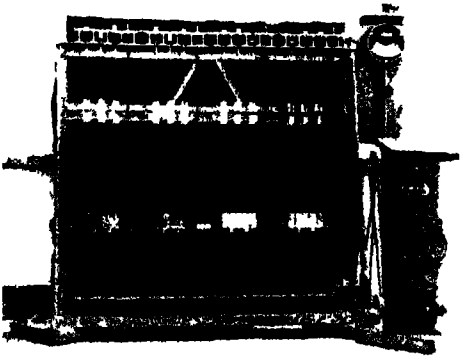


Fig 92 —Oxley's apparatus

pushed to fasten the cloth between the jaws Between these jaws is a steel plate E with a brass guide bar against which the cloth is placed to ensure its being evenly and correctly set The test is performed as follows Place the material on the plate E taking care that the ends are evenly placed beneath the jaws B Then secure it by pushing over the lever C Before securing the second it is necessary to see that the cloth has an even tension by pushing it under the second jaw without any unevenness When this has been done, secure the end by means of the lever D, and apply the power at K By means of the screw Q a strain is put upon the material till it breaks, the pointer indicating on the dial the number of pounds at which it broke, and the indicator F the elongation before breaking

The Bursting and Ripping Strain of Fabrics.– Hubner (*J Soc Dyers and Col*, 1921, p 71) states that the resistance of a fabric to "bursting" or to "ripping" affords often, valuable information, and, in many cases, a bursting or ripping test can replace the more tedious tensile test In paper testing, the bursting strain is frequently considered a suitable criterion of strength and quality For the ripping test Hübner employs a "Schopper" paper-testing apparatus His method consists of cutting either the warp or weft threads

to a depth of 2 inches, then fixing one end of the cut piece in the upper and the other end in the lower jaw of the machine The jaws are made to move apart at a uniform speed of 3 inches per minute, for a distance of about 2 inches, and the strain is applied at right angles to the threads to be broken The bursting strain is measured by a "Mullen" paper-testing machine, in which the paper is burst by means of an inflated rubber diaphragm Many interesting applications of these tests are given in the original paper

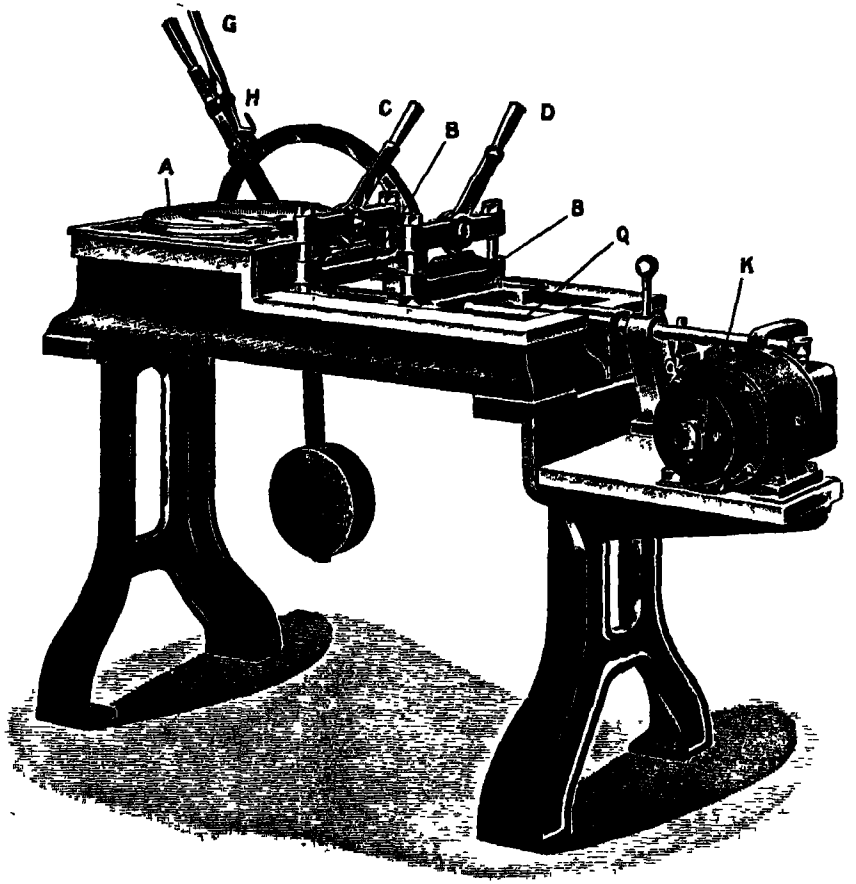


FIG 93 —Cloth-testing machine

Measurement of Twist.—The twist of a yarn is the number of complete turns which it makes in a given length, generally 1 inch It is measured by means of the machine shown in fig 94, which records the number of turns necessary to untwist the yarn A is a dial, which is rotated by a screw crank BC, connected with the wheel B. It is engraved with figures showing the number of revolutions made The pillar is clamped to the board by means of a screw clamp at any required distance To make a test, the nut on the dial is loosened and the dial is set at zero, after which the nut is screwed back. The yarn is fixed by means of the clamps, the pillar being moved outwards till the yarn is

just taut, but without undue tension The pillar is then clamped on to the board and the handle turned until the yarn is free from twist The number of revolutions made by the wheel is then read on the dial, and this, divided by the length of yarn tested, in inches, gives the number of turns per inch

In dealing with folded yarns, we have two kinds of twist which may be in opposite directions These are (1) the twist imparted to the fibres of the single yarn during spinning, and (2) the twist introduced in folding the single yarn into a double or threefold thread The length usually taken for measuring twist is from 4 to 6 inches, but the accuracy of the test varies inversely with the length We have already noticed the great variation found in twist from inch to inch of a yarn It is only when a considerable length, such as 6 inches is taken that any approach to regularity appears Inasmuch as the tensile strength of a yarn is very closely connected with the regularity of the twist, tests should always be made upon a short length such as 1 inch or

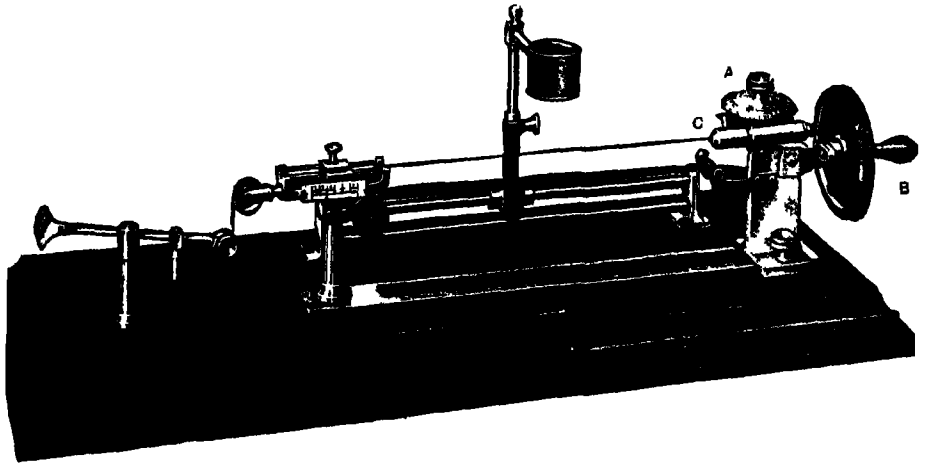


FIG 94 — Goodbrand's twist testing machine

even ½ inch The important fact to ascertain is not the average twist over a long length but the maximum and minimum from inch to inch, and the frequency with which excess or deficiency in twist occurs If a yarn were prepared from perfectly combed fibres of uniform diameter with perfect machines, the twist would be practically constant throughout In practice this ideal cannot be attained, but good yarns approach the ideal more closely than bad ones Thus, in the examples given above we see that in one case the twist varies from 10 to 60 The chief cause of variations in twist is irregularity in the diameter of the fibres When coarse and fine fibres are mixed, the finer fibres take the twist at the expense of the coarser ones In order to put enough twist into the coarse fibres we must overtwist the fine fibres Deficiency in twist makes a yarn weak, because the fibres are easily pulled apart, especially if they are short Excessive twist destroys elasticity and causes yarn to snap when subjected to tension It also tends to form little knots which catch in machines and break Finally, sufficient twist would actually rupture the fibres

We have seen above that the twist of a yarn bears a definite relation to its count For cotton and worsted yarns the figures are—

	Warp Yarns	Weft Yarns
Cotton	Square root of count multiplied by 3 75.	Square root of count multiplied by 3 25

A twist much in excess of the theoretical value causes the yarn to form kinks, which limit its elasticity and catch in machinery In doubled yarns the component threads are twisted together in the opposite direction to that of the original twist of the threads The evenness or regularity of a yarn may be judged by winding it off on a flat board or card and examining it with a lens Inequalities, knots, etc , may be detected by this means

The Analysis of Cotton.

The special tests for bleached cotton will be described later (Chapter XXIV). The present section deals only with the general analysis of an unbleached specimen It is frequently of importance to a bleacher to know the composition of a sample which he has to deal with The routine tests include the determination of

1 Moisture
2 Mineral matter or ash
3 Oil and wax
4 Matters soluble in boiling sodium hydroxide solution after removal of oil and wax
5 Colouring matters removable by bleaching

Determination of Moisture. —Moisture is best determined by the method described under "Conditioning" If no conditioning oven is available, the following alternative process may be used About 5 grammes of the sample are weighed accurately in a wide mouthed stoppered weighing bottle The stopper is removed and the bottle and its contents placed in an oven heated to a temperature of about 105° C After two hours the bottle is removed, cooled in a desiccator, and weighed after insertion of the stopper It is then heated in the oven again for half an hour and weighed, the process being repeated till no further loss of weight occurs The total loss is the water present in the weight of the sample taken

Determination of Mineral Matter or Ash.—About 5 grammes of the sample are weighed in a previously weighed platinum, silica, or silver dish The dish is then ignited over a Bunsen flame or in a muffle till a white or greyish ash is obtained It is then cooled in a desiccator and weighed

Oil and Wax.—The dry residue obtained in the determination of moisture may be used It is placed in the chamber of a Soxhlet or continuous hot extractor The latter is preferable The apparatus has been described on p 76 A suitable solvent, such as chloroform, carbon tetrachloride, or benzol, is placed in the weighed flask and the liquid kept boiling for about three hours The solvent is then evaporated off and the residue in the flask dried to constant weight and weighed This gives the total fatty matter If further details are required it may be examined in the following way—

Free fatty acids may be determined by adding a little neutralised industrial spirit to the flask, warming the mixture to dissolve the free acids, and then titrating carefully with decinormal sodium hydroxide, using phenolphthalein as indicator The first appearance of a permanent pink colour indicates the end

point of the reaction This colour disappears if the mixture is allowed to stand, since any excess of free sodium hydroxide saponifies some of the fat Each cubic centimetre of decinormal alkali used neutralises 0 0282 gramme of oleic acid, in terms of which the free fatty acids are expressed

Unsaponifiable Matter.—A little more spirit is added after neutralising the free fatty acids, together with about 2 grammes of solid potassium hydroxide (or 5 c c of a 50 per cent solution) The flask is attached to a vertical condenser and heated on a water-bath for two hours, with occasional rotation of its contents A long glass tube, of about half an inch diameter, forms a satisfactory condenser At the end of two hours the mixture is poured into a separating funnel (fig 95) The flask is washed out two or three times with small quantities of hot distilled water, the washings being added to the contents of the separating funnel After allowing these to cool, about 25 c c of ether or petroleum ether are placed in the flask and rotated to dissolve any residual fatty matters It is then poured from the flask into the separating funnel, the stopper is replaced, and the contents of the separator well mixed by shaking or rotating of the funnel, in order to dissolve the unsaponifiable matter After standing for a short time the solvent will rise to the surface, forming a clear layer containing the dissolved matter If an emulsion be formed, or if the solvent does not separate completely more spirit should be added and mixed with the liquid in the funnel The lower layer is now drawn off carefully, the stopper having first been removed The ether is washed twice in the separating funnel with a little distilled water and a few drops of alcohol It is then decanted through the mouth of the funnel into a dry weighed flask The lower aqueous layer is returned to the separating funnel and the extraction repeated The combined ether extracts are then evaporated, the residue dried in the oven and weighed



Fig 95.—Separator

Matters Soluble in Sodium-hydroxide Solution. After extraction with ether the cotton is dried and weighed in the stoppered weighing bottle as described above It is then placed in a flask containing a 2 per cent solution of sodium hydrate The flask is connected with a reflux condenser and its contents boiled gently for three hours After this, the liquid is poured off and the cotton washed rapidly several times with hot water, and then with cold water till it is no longer alkaline in reaction It is then rinsed with dilute acetic acid (0 5 per cent) to remove the last traces of alkali, washed again with water, dried, and weighed in the bottle The difference between the weights before and after boiling gives the amount of matter soluble in sodium hydroxide The matters soluble in alkali are often determined on the original sample without previous extraction with ether and alcohol In this case they include, with the pectins, proteins, etc, much of the oil, wax and colouring matters When this direct determination is required, a small autoclave should be used, as the saponification of oil by means of dilute alkalis is very slow at 100° C

Loss Due to Bleaching. The dry boiled cotton from the above experiment is next treated with chlorine water till completely bleached The chlorine water should contain about 1 gramme of chlorine per litre

A faintly acid solution of sodium hypochlorite of a density of ½° to 1° Tw may be used instead of chlorine water, and the time may be shortened by warming it to about 30° C After bleaching the cotton is washed with water and then

with water containing a little sodium sulphite to remove the last traces of chlorine. Finally it is washed again with water, dried, and weighed The loss in weight gives the matters removed by bleaching.

The following is an example of the results obtained from an average sample of cotton yarn by these methods, the results being expressed as percentages on the dry material:—

Oil and wax	0 75
Matter soluble in sodium hydroxide	6 55
Loss on bleaching	0 78
Mineral matter	0 12

CHAPTER XIV

COTTON PIECE GOODS (Introductory).

THE bleaching of cotton piece goods constitutes the largest branch of the bleaching industry, and comprises in the wider sense of the term both the scouring and bleaching of the grey cloth, thus preparing it for the subsequent processes of printing, dyeing, or finishing. The requirements of each of these processes vary considerably in respect of the degree to which it is necessary to remove from the cloth those ingredients which render it other than pure cellulose. These include (1) impurities introduced in the sizing of the yarn before weaving, or applied to the cloth after it was woven, (2) "motes" or particles of the husk of the cotton plant, (3) the natural impurities occurring in the fibre. The presence of the first named, together with the mechanical difficulty of penetrating the more or less closely woven cloth, and the necessity for handling large quantities of considerable length in a practicable manner, especially distinguish the art of piece goods bleaching from other branches of the industry.

Printers and Dyers. In preparing piece goods for calico printers, the extreme requirements to be complied with (relating especially to the printing of coloured patterns on a white groundwork and when the ageing process is employed) are, that the cloth must be thoroughly bottomed or freed from all impurities which tend to prevent it from accepting a clear and well defined impression. Also, that the cotton must be entirely free from conversion into oxycellulose, as this would be turned to a brown colour during the ageing process, and the white ground be spoiled. The presence of oxycellulose is also detrimental to the uniform reception of certain dyes, when occurring even in the least traces. Under less onerous conditions, as when a white ground is not required, the bleaching process is not carried to its extreme limits of safety, while, if the colour to be printed or dyed be of a dark shade, the process may frequently be confined to that of merely scouring, and the chemicking omitted, as, for instance in the turkey-red bleach, wherein it is of extreme importance to avoid the least risk of oxycellulose.

In general, for printers and dyers, the first consideration is the absence of all fatty and resinous matter, so that the cloth is highly and uniformly absorbent. Secondly that it is practically free from oxycellulose, and as white as may be desired, whether it be for a pure white ground, or for enhancing the brilliance of a delicate shade of colour, or that the whiteness of the cloth has not sufficient influence on the shade in question to warrant the cost of obtaining a good white, or indeed anything better than is produced by scouring.

Finishers.—In the white trade, for the production of a bright, permanent, well-bottomed white, it is necessary that the scouring and bleaching process shall have effectually operated throughout the fibre, otherwise the cloth will be lacking in brilliance of tone and capacity to acquire the physical properties which should result from the application of the various finishing processes.

Thus cloth of a given quality must be rendered uniform in its capacity for absorbing and retaining moisture, the presence of which in correct proportion has a most important bearing on the effect produced by beetling, calendering, etc It must similarly be readily absorbent to the stiffening, weighting, tinting, and other ingredients applied in finishing The general chemical processes of boiling, bleaching, and scouring will be dealt with later, but their significance in the treatment of cotton is assumed to be understood For the present, attention will be directed more particularly to the consideration and significance of cleansing and bleaching as distinctive treatments, the former relating generally to the removal of the resinous and other impurities, and "bleaching" to the decolorising action induced by oxidising agents

Cleansing.—The significance of thorough cleansing is perhaps best regarded from the standpoint of the bleacher, and it is hardly an exaggeration to state that his task is practically accomplished when the cloth has successfully reached the stage when it is ready for "bleaching" or rendering white by submitting it to the action of an oxidising agent Any local irregularity of action occurring in the preliminary stages of decomposing and dissolving the sizing and natural impurities can hardly be remedied Such defects will be largely detected during bleaching and souring, as stains which may, in favourable cases, submit to localised treatment, but will in all probability result in subsequent trouble, both as regards the colour and finish of the goods

The student who would aim at producing the most perfect work must therefore limit his dependence on that part of the process, which would at first appear to be the most rapid and effectual, as undue reliance on the oxidising process leads to oxycellulose and tendered cloth, and fictitious and temporary whiteness, which passing away, can be brought back neither by blueing nor rebleaching

Owing to exigencies of speed and economy, the experienced bleacher may occasionally ignore the above contention when bleaching for the white trade, as a moderate degree of over bleaching may pass muster without detection by the customer but in any case he should take no risks in failing to secure the removal of any residual traces of the bleaching or souring agents, as these are even more detrimental in their subsequent effects when concentrated by drying than when used prematurely or too liberally on the wet cloth

When bleaching goods interwoven with coloured patterns, the omission or suppression of the boiling process is more generally called for, to preserve the coloured portions, hence it will be seen that even the most generally applicable precautions and rules are subject to exceptions In further illustration of such exceptions, one may refer to a case in which resinous matter is deliberately introduced into the material towards the end of the process to obtain certain physical results affecting the finished appearance of the cloth, such as roughness and stiffness, and again to give body to the fibre and the property, after partial drying or "conditioning," of modifying the effect of calendering to imitate closely that produced by the more costly process of beetling

Despite the difficulty in enunciating rules of quite universal application, the art may be studied on broad lines, and principles arrived at to assist the judgment in dealing with and appreciating the conditions applicable to individual cases, although the element of personal judgment must necessarily play an important part in devising the best mode of procedure in specific cases

Thus the art of bleaching consists in adapting the number, duration, and severity of a series of known processes to the requirements of an assortment of dissimilar goods, which, for reasons of economy, must be handled in bulk with due regard to unequal capacity to withstand a common treatment

Checking.—On receipt of the grey cloth, it is examined by means of samples selected at random from a given batch, and of these the length, width, weight, and count are tested, and the results recorded in the "Grey Book" The cloth usually arrives in "lumps," or pieces plaited (or folded lengthwise) in laps of nearly uniform length Several measurements of these are taken, averaged, and multiplied by the number of laps to get the gross length of the piece

Storing.— The bulk is then piled for storage on clean wooden grids or "stillages," slightly elevated from the ground by cross bearers, and the piling effected so as to afford the best possible ventilation through the bulk, and occasionally rearranged, to prevent the formation of mildew

Assortment.—By reference to the Grey Book suitable assortments are made, constituting a convement batch of goods of approximate similarity for treatment by a common process in bulk, and assembled in due sequence

Stamping.—The ends being drawn out, they are successively moved over a stamping table, where, with a hand stamp and gas tar, they are marked for



Fig 96 Donkey stitching machine

subsequent identification, and passed thence before the stitching machine, and the leading and tail ends of consecutive pieces stitched together, so that the face sides will be in the same plane They are then deposited so that a continuous rope or band can be drawn off, according as they proceed direct to the croft or require singeing

Stitching. The simplest device, known as the donkey stitching machine, consists of a base plate supporting a bracket and hinged arm (fig 96) The bracket carries a stud, on which revolves a toothed wheel, gearing with a similar one attached to the overhanging hinged arm These wheels are rotated by a hand wheel, and when two ends of cloth are engaged between them, they are gathered into a series of loops Midway between the wheels, and lying within intersecting circular grooves cut in the teeth of the feed wheels, lies the free pointed end of a threaded needle, supported endwise by a spring buffer or stop Hence in the passage and looping of the cloth accompanying rotation of the feed wheel, it is threaded on to the needle, which can be drawn by hand, with its thread following, to effect a gathered stitch connecting two pieces They are then stretched out and the ends of the thread secured This mode of connecting is simple, and fairly rapid, and gives a strong stitch, which can be readily with-

drawn, if required, to disconnect the pieces The method is also easily imitated by hand in remaking the joint The needles can be duplicated for stronger joints, by cutting two grooves in each feed wheel, and the joint may be made to lap, or abut, according to the method of feeding the ends to the machine The more usual practice is to employ a modern chain-stitch machine (fig 97), mounted

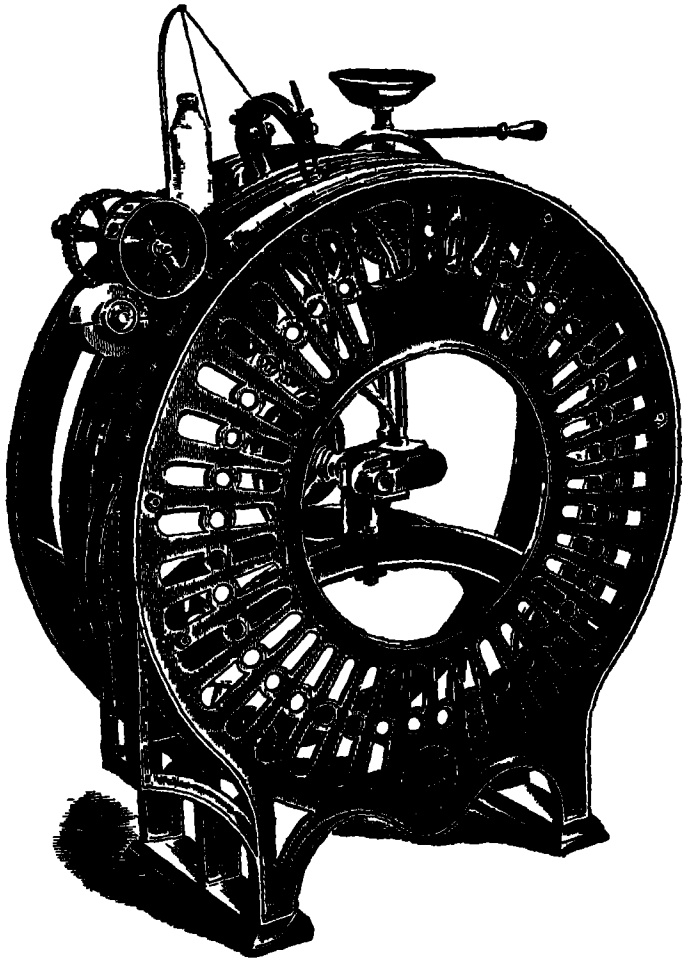


Fig 97 —Rotary stitching machine.

in conjunction with a special feeding and trimming device, consisting of a frame about which revolves a steel band, studded with spikes upon which the " ends " are impaled during its revolution, and carried by it past the stitching machine and thereby stitched together endwise. Release from the spikes is effected by the interposition between cloth and machine of an inclined forked spring, with slits for the reception of the spikes. A circular cutter trims off the superfluous edge of the stitched joint

Singeing.—The singeing process is introduced at this stage for convenience,

as the cloth is about to be washed, etc. Its object being to dress the face of the cloth or burn off the nap left by the manufacturer, does not concern the

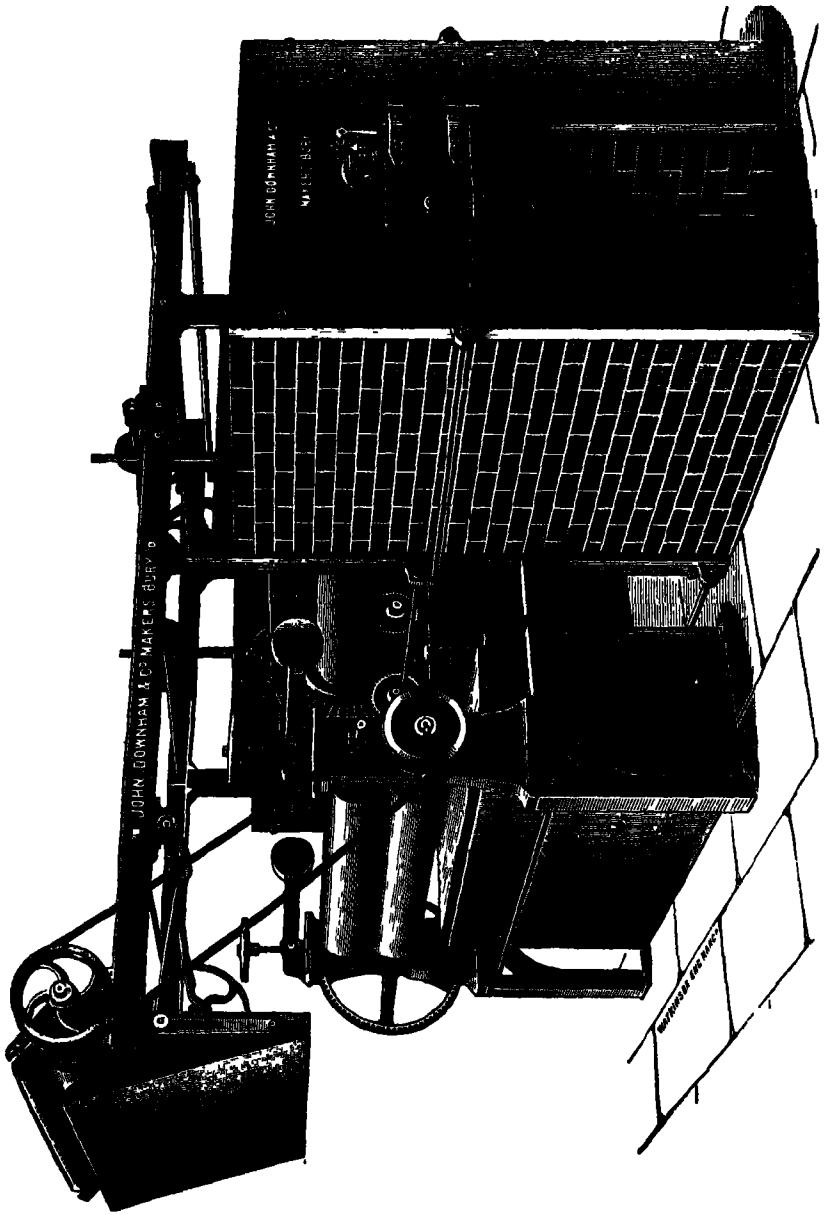


FIG 98.—Singeing machine

bleaching, except that it affords an opportunity of detecting the presence of injurious ingredients, which may be exposed by the concentrating action of applied heat.

It is further of interest to the bleacher in that the passage of the cloth over the plate assists to some extent in the destruction of motes, etc , which happen to come in contact with the plate, and are thereby more readily removed in the later stage This process also attacks the particles or wads of black swarf which are found embedded in the fabric. They are caused during weaving, and contain mineral oils and dirt, which it is almost impossible to extract in the bleaching process

The process involves risk of burning the cloth and introducing similar defects to those of kier burns and over-bleaching The distinguishing feature lies in the occurrence of such defects in a direction parallel to the length of the cloth, and hence dissimilar to those occurring while the cloth is in the rope form

The machine (fig 98) consists essentially of a copper plate slightly barrelled and of circular or ∩-shaped section, set in fireclay, with an arrangement for longitudinal expansion, and forming the crown of a horizontal flue, leading from a coke furnace or an oil jet, and heated thereby to a uniform red heat. Over this the cloth is drawn in open width by the rollers of a wetting-out mangle, run at adjustable speed, and guided to the requisite degree of contact by means of guide rods capable of adjustment and rapid release by a hand lever. The plate singeing may be supplemented by gas singeing, or the latter used alternately for lighter duties This consists of one or more Bunsen burners giving a continuous flat vertical flame, produced by gas, and forced air draught produced by a fan The flame issues from a narrow orifice which is adjustable both as regards width and thickness The cloth passes under a water-cooled roller, and the flame impinges on its under surface during its momentary passage, singeing the nap without attacking the surface of the cloth to any appreciable extent

The main precautions to observe in singeing are to adjust the speed of transmission of the cloth over the burner or plate to suit the amount of singeing to be done, without risk of burning the cloth The plate must be kept smooth and its contact with the cloth be uniformly even, and as the plate is liable to distortion under expansion and contraction, the setting must be carefully and evenly performed, so as to avoid twisting or humping the plate through resistance to longitudinal expansion or access of cold air by leakage in the setting.

A slight barrelling of the plate is desirable to produce uniform contact by taking out creases, and for the same purpose the cloth is subjected to a slight tension at the feeding end by passing over tension rails The first piece is sewn to a fent threaded up by means of a tape, so that the proper adjustment of flame, or guide rods, may be made before the actual cloth to be singed enters the machine

CHAPTER XV.

STEEPING.

THE next process is that of steeping, which has for its object the softening and opening up of the fibre preparatory to boiling with lime or caustic soda. The goods are, thus, rendered more permeable and the action of the lye is assisted Further, steeping aids in the removal of sizing materials by promoting the conversion of starch into soluble starch, sugar, or dextrin by means of natural fermentation

The simplest form of steeping is where water alone is used The goods are wetted down and covered with water at a temperature which promotes the multiplication of the organisms naturally present on the goods or in the water. A temperature of about 100° F is suitable Any convenient vessel, preferably of wood, may be used, the goods being run in from a washing machine, to ensure saturation and loose plaiting down of the material

At a temperature of 100° F the organisms present multiply rapidly. Many of them secrete enzymes capable of liquefying starch or proteins. Thus, the sizing matter passes into solution gradually, and can be removed by washing This makes the next process, *i e* lye boiling, easier It has been noted above that cotton contains mineral and other impurities which are comparatively readily soluble in water, and which would also be removed Great care must be taken to prevent the liquor from becoming foul or mouldy, and to minimise this risk the water must be changed frequently. Polluted water should not be used, since it contains, often, putrefactive or chromogenic organisms, which attack and damage the cotton, causing tenderness or coloured spots, the latter being difficult to remove subsequently If the operation be conducted with care the results are quite satisfactory, and there is but little danger of damaging the fibre The process generally takes a day to complete, this corresponding to the period between the successive charges of the grey-boiling kiers, but in practice, sometimes, for the sake of convenience, it is allowed to extend over the week end In this case the liquor often becomes turbid and emits an offensive smell This is dangerous, and indicates that the action is proceeding too far Owing to the time and extra space required, steeping is frequently omitted, or replaced by shorter process, such as wetting out in a water mangle attached to the singeing machine, and steeping by simply piling the wet goods overnight

The removal of starch dressing or sizing is much more complete if an amylolytic enzyme is used Diastase, malt extract, or a commercial preparation of diastase, such as diastafor, may be employed About 0·05 to 0 1 per cent of this is mixed with water in the steeping bath. The goods are entered and the temperature raised to about 65° C. The diastase converts the starch into a mixture of maltose and dextrin, both of which are readily soluble in water and can therefore be washed away It must be remembered that the action of diastase is completely inhibited by alkalis

Animal amylolytic enzymes are more powerful in their action than those from

vegetable tissues, and have the advantage that they can be used at higher temperatures. "Rapidase," an enzyme obtained from *Bacillus subtilis*, is similar in properties. It can be used, either in a neutral bath, or one containing soap or sodium carbonate, half a pound of sodium carbonate and 5 lbs. of soap per 1000 gallons do not affect its activity Thus, a certain amount of scouring may be effected simultaneously with the desizing. The process is carried out as follows: The cloth is wetted out in water at 176° to 185° F. and then impregnated in the rapidase bath at 185° F. The goods are then rinsed in water at a temperature of 203° F. in a washing mangle The quantity of rapidase used varies from 3 to 15 lbs per 100 gallons, depending upon the amount of liquor remaining in the goods after squeezing The cloth is run over four or five rollers in the rapidase bath and then into a washing machine supplied with hot water In this way continuous desizing is obtained

Among other methods are (1) the use of an old soda lye liquor, and (2) a wash through or a soak in acid The latter is found to exercise a disintegrating effect on the impurities in the cloth, and is, for example, introduced in this connection as a scouring agent in the dollying of lace goods of exceptional dirtiness and also in the Thies-Herzig process

Soaking in dilute hydrochloric acid, followed by washing, is very advantageous, particularly if the acid is used lukewarm at a concentration of from 0·5° to 1° Tw This is the case when an ash-free fabric is required The effect of an acid soak on the mineral matter is illustrated by the following example —

	No 1	No 2
	Per cent	Per cent.
Ash in original yarn . .	1 17	0 94
Ash after soaking in water .	0 28	0 27
Ash after soaking in warm hydrochloric acid (1° Tw) .	0 08	0 13

If an ash-free cotton be required, the proper course is to remove the mineral matter at the outset, and not from the bleached goods as is commonly done The same remark applies to ramie, which is much used for incandescent gas mantles

CHAPTER XVI.

TRANSMISSION OF CLOTH—IMPREGNATION AND PLAITING.

Transmission of Cloth.—The handling of cloth in its passage through the process following singeing is usually effected in the "rope" form, the method of treatment in the open width being, however, adopted when it is necessary to maintain a maximum width and avoid creases and distortion of the weft threads The latter process is employed by some calico printers, and is claimed to produce a more uniform result, both as regards regularity of the texture and colour Transmission in the rope form is more convenient, and the apparatus for boiling and bleaching, etc , is cheaper and occupies less space for a given output, and the results obtained satisfy practically all requirements

The distinction between the open width and rope formation is that, whereas in the former the cloth is either passed over rollers or wound and unwound in rolls or "batches," no attempt is made in the latter to maintain the cloth in its original or open width, the ends being gathered up and threaded through glazed earthenware "pot-eyes" (fig 99) or guide rings, and in the course of its transmission in this form it is soon subjected to a series of spiral twists. If such a rope be opened out at any stage, it will generally be found that one selvage lies ahead of the others, so that the warp threads lie diagonally between the two. This is remedied after the cloth leaves the croft, the cloth being opened out in a "scutcher" (see fig 100), and the weft threads straightened by the application of tension or drag on the leading selvage as the cloth is led into the "first time" water mangle at the commencement of the finishing process Similar rectification is applied, if required, during subsequent processes, and there are also special appliances, such as the weft straightening machine and the jig stenter, whose functions are in a primary or subsidiary measure devoted to this end

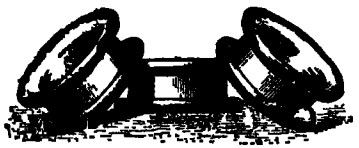


Fig 99.—Pot-eyes

Recovery of Width.—The recovery of width, always lost during a longitudinal stretching of the cloth is also effected during the finishing processes by a variety of operations which do not concern us at this point, but amongst which may be mentioned the scrimp rail and various forms of rotatory expanders developed from it, also the belt or clip-stretching machine, and the stenter Increase of width is also an effect incidental to the process of beetling.

Transmission.—The method of transmitting the rope from process to process is by means of washing machines (fig 101), winces, and pot-eyes The washing machine is essentially a pair of rollers surmounting a water beck or box provided with means for agitating the cloth in its contact with the water. The

rollers incidentally serve the purpose of drawing the cloth to the machine and through it The cloth is threaded and dragged through a series of glazed earthenware rings or pot-eyes which direct its course, being fixed in suitable number and conveniently disposed about the bleach croft to admit of any desired grouping or "runs." The passage of the cloth is continued beyond the washing machine by means of winces or drums consisting of six or eight wooden lags, mounted on the shaft by means of rings carrying peripheral lugs (fig. 102), to which the lags are bolted. These winces are driven so that their peripheral speed exceeds that of the washing-machine rollers by 10 to 15 per cent., and the

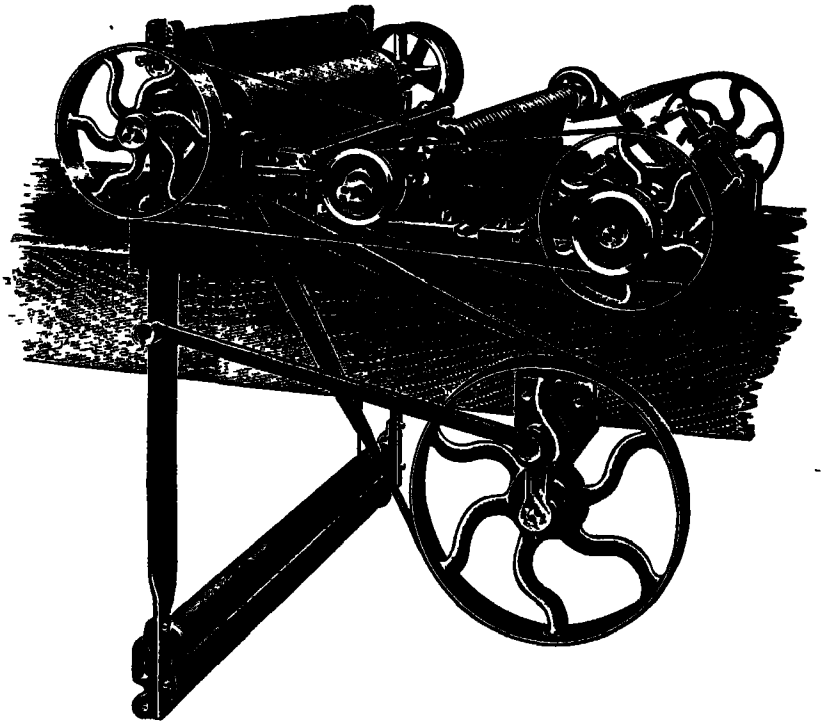


Fig 100.—Scutcher

transmission of the cloth over these is effected by the friction existing between the wince and the cloth This depends upon the arc of contact between the two, and on the tension applied at the extremities of the cloth during the contact If that on the delivering side be inadequate (as when a short end hangs over the wince and the other is detained by hand), the wince will not deliver. Hence to effect delivery of a free end (as to a stillage or kier) the dependent weight and therefore length of drop must be sufficient to effect the necessary driving power

To increase the driving power of a wince one may increase the arc of contact by coiling the cloth completely round the wince, though this is rather apt to cause a mishap, unless the leading end be carefully guided. To meet the contingency of the cloth wrapping round the winces, which can cause bad damage very quickly, the driving shafts should be controlled by friction clutches to allow

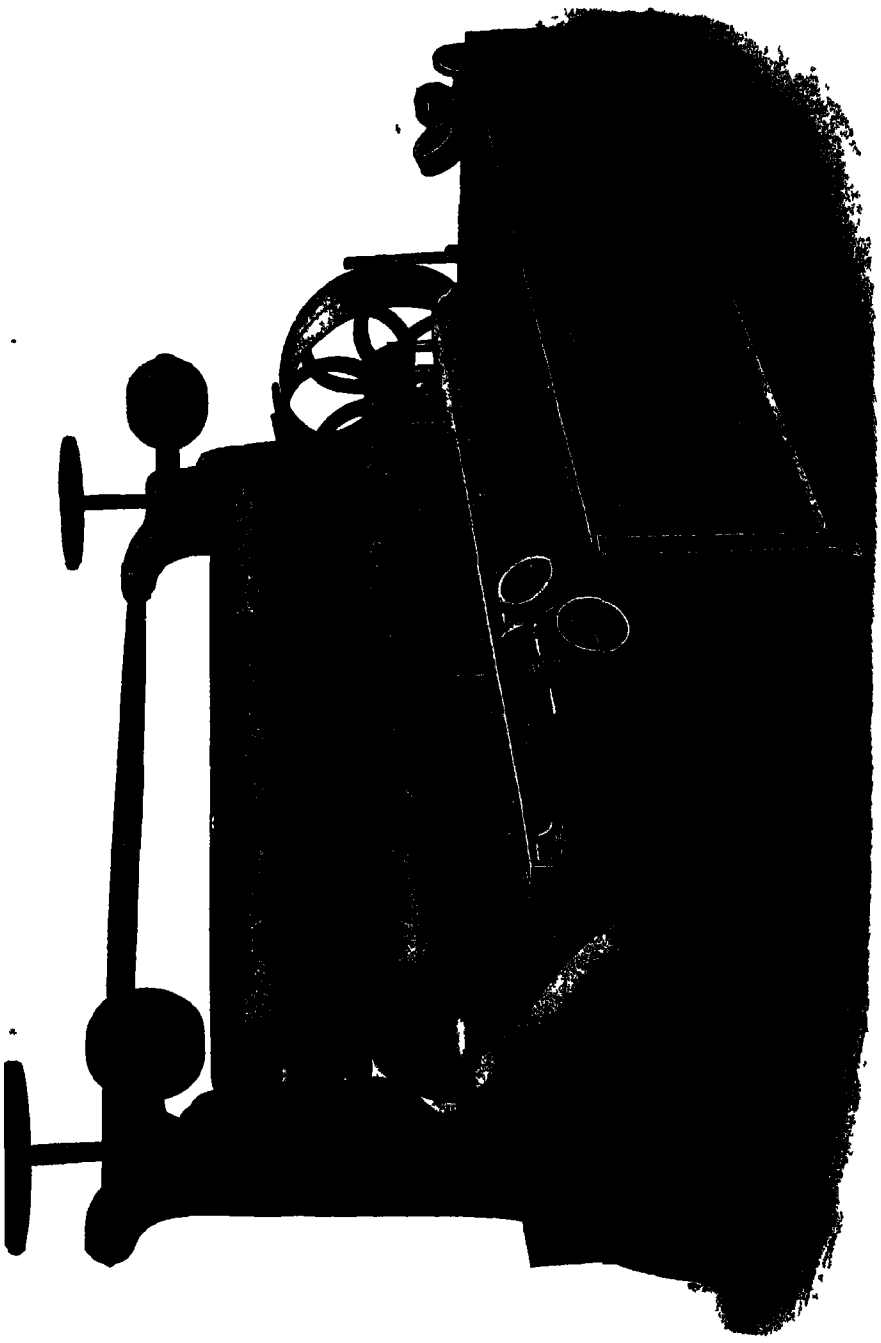


FIG 101.—Roller washing machine.

of instant disengagement. Laps of cloth are sometimes trapped between the wince lags, so these are generally boxed in. The shafts should be well protected with paint to avoid rusty water dropping on to the cloth, and the hangers should be supplied with efficient oil-catchers Dirt stains are a frequent cause of trouble, and every means should be adopted to anticipate and prevent their occurrence.

An automatic mechanism for preventing accidental damage to goods by trapping or lapping, when passing over a wince at a rapid rate, has been patented

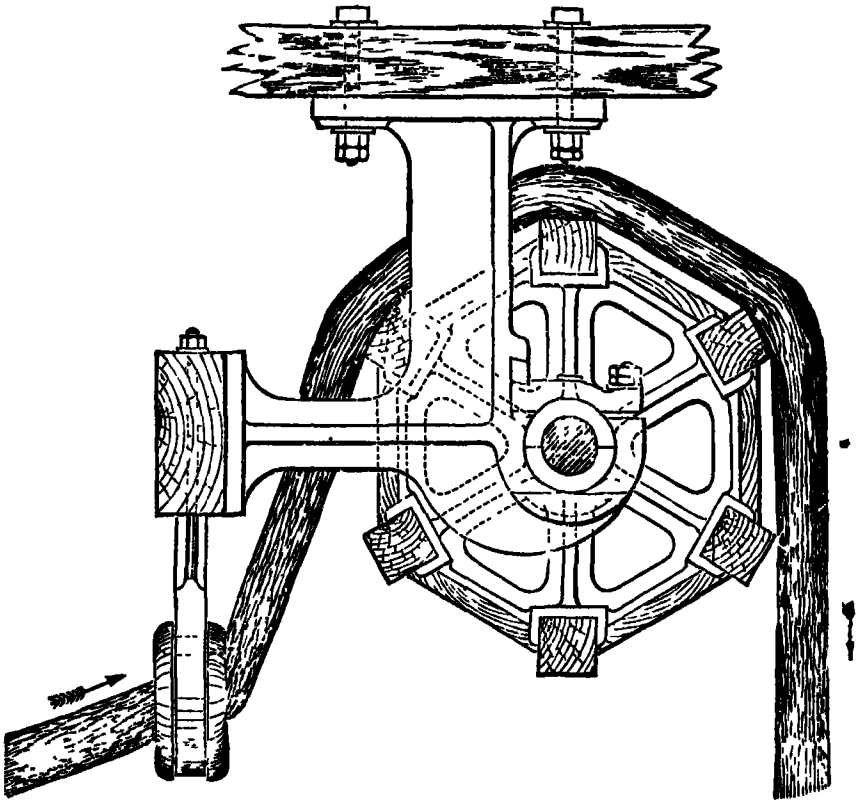


FIG 102 —Wince

by the Bleacher's Association, Ltd (*J Soc Dyers and Col*, 1922, p 301) A sectional end elevation is shown in fig 103 (1) represents the wince, (2) the material passing over in the direction of the arrow On an adjacent beam (3) are fixed two brackets (4), supporting a shaft (6). Two or more swinging levers (7) carry upon their upper and lower extremities respectively bars (8 and 9) with serrated or sharp edges The levers normally swing free of the fabric, which, if caught, swings the levers over as indicated by the dotted lines, the sharp edge (9) severing the fabric.

Tension.—An important matter in the threading up of runs in a croft is the adjustment of suitable tensions, for, as the cloth is drawn through the pot-eyes by the washing machine, there occurs the opportunity of effecting the

required stretch which must be imparted to the cloth to lengthen it This effect is spread out through the series of runs occurring between the various stages of the process But judgment is required to apply sufficient tension without damaging or fraying the cloth The longer and more numerous the runs, the easier will it be to produce the required length, but failing adequate length, an additional tension must be introduced by means of the pot-eyes, which must be placed so as to put frictional tension on the cloth A series of three adjacent pot-eyes fixed on adjustable brackets, at the entrance to the washing machine, for instance, may be employed to vary the tension imparted between this point and the final nip of the machine, but the more rational position for such a device, and where the angular adjustment may be more moderate, is at the other end of the run feeding the machine, so that the stretch would be distributed over a greater length of material The friction applicable to the wince runnings is limited by their driving power, and, in any case, that is not the right place to apply abnormal tension, as the winces are sufficiently apt to fray the cloth without additional inducement, so friction in that direction must be reduced to a minimum The production of an artificial tension and its application to a short length of cloth are on the whole not to be recommended If the croft be a short one, it is better to extend the runs artificially, there being no serious objection to taking the cloth round corners, provided that a jockey roller be used at the bend between two pot-eyes The transmission of light goods, having considerable length in proportion to weight, may conveniently be run two- or fourfold, to expedite their handling The final subdivision is effected by separating two ends at a time and running these through two pot-eyes in the washing or squeezing machine, and allowing 6 feet or as much more as possible between these two pot eyes and that from which the bifurcation commences If the available distance be short, a dividing roller is placed between the pot eyes to assist separation of the ends

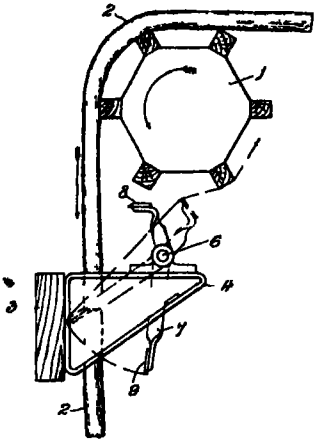


Fig 103 Automatic wince

When a rope of impregnated or dirty cloth crosses the path of another run, the two must be parted by pot eyes or staves, and the one which is liable to damage by contact with the other run uppermost

Tandem Running.—It is sometimes convenient to thread up a run, so that the cloth passes through two machines in tandem In such case the machines must either be geared to run at the same peripheral bowl speed (which is difficult, on account of the wear of the bowls), or a length of slack cloth must be allowed to sag between them to allow a margin of time for effecting relative adjustments of speed, or stoppage without damage to this intervening length If the space for such an arrangement be limited, the sag may be accommodated by a compensating roller or weighted jockey pulley sliding in a long vertical groove, but there can generally be found some stillage to which the loop may be dropped and then guided to the next machine through pot eyes If this be some distance from the machine, it is watched by a boy who gives the necessary signals to the machine-minders by means of a whistle used in accordance with a familiar code. Such means of rapid signalling between the platters and machine-minders is also

customary to give advance information of such occurrences during the passage of the cloth as demand special manipulation of the machines, in respect of knots, headings, ends, etc.

Impregnation and Circulation.—Having dealt with the preparatory treatment of piece goods and their mode of transmission, we must now refer to certain characteristic appliances and operations for bringing the various liquors employed in the processes of boiling, bleaching, souring, and washing into most effectual and uniform relationship with the cloth, and at suitable concentration and temperature

As several of these operations are conducted with the cloth in bulk (*i e.* in a stationary condition) and only the liquor in motion, it is necessary to ensure very uniform impregnation, packing of the goods, and circulation of the liquor.

The treatment in bulk is confined to processes requiring some considerable time for their completion, and these stationary processes are alternated with others involving the motion of the cloth through washing machines in the manner already described in connection with the transmission of cloth. The object of such intermediate or preparatory mutations of the cloth is either its washing, or its impregnation with the liquor with which it is desired to saturate it, to facilitate regularity of treatment in a stationary process.

Thus, by means of these processes, during which the cloth is transferred from one vessel and process to another, not only must the saturation of the cloth with the required liquor be rendered uniform, but the cloth must be freed, by washing, from the residue left in it as the result of the completed stationary process, and undesirable reactions between the successive reagents prevented.

It is, in fact, only in virtue of these intermediate mechanical washings, and occasionally through the superior degree of saturation effected by impregnation, that the stationary processes become practicable

The machine most usually employed for either purpose is that shown in fig 104, which fully satisfies the requirements for impregnating. The process of mechanical impregnation is adopted (1) when the quality or state of the cloth renders it very impermeable to saturation, as, for instance, when manufactured with stout and closely woven yarn, and while the impurities are as yet unattacked and add to the difficulty of effecting saturation; (2) when the liquor to be applied is not a clear solution, but, as in the case of lime water, a thick turbid mixture containing large quantities of insoluble matter held in suspension, to which the cloth would merely act as a filter if the method of gravitational circulation were applied without preliminary impregnation.

Examples of the method of impregnation occur in the "liming" of cloth preparatory to the lime boil, and in the "lime sour" subsequent to this boil, the reason for the former process being due especially to case (2) above mentioned, and resulting in the impression of the liquor and its suspended solids into the body of the cloth as it passes in sequence through the liquor and the rollers of the machine, which serve alike to transmit and squeeze the cloth. When liming by means of a washing machine, instead of the usual supply of water into the box of the washing machine (as its function is now that of impregnating), a pipe is run from an adjacent tank in which the lime liquor is contained, the sediment is stirred up with a paddle to produce a liquor of the consistency of buttermilk, more or less, according to the judgment of the bleacher and the strength of boil determined upon. Into this machine is fed a stream of water which causes an overflow of the milk of lime through the outlet pipe into the box of the liming machine. It is important that a sieve be inserted in this outlet to prevent the discharge of grit and particles of unslaked lime.



FIG 104.—Saturating machine

The agitation in the preparing tank must be maintained so as to yield a liquor of uniform consistency

Sufficient agitation of the liquor in the liming machine is effected by the swirl of the cloth round the wince rollers in the box; and excess of liquor is squeezed out of the cloth at the final nip between the driving rollers as the cloth then passes to the kier.

Impregnation preparatory to boiling in alkaline lyes is of less importance and generally omitted, as these percolate through the cloth without its having a filtering effect on their soluble constituents

Impregnation with the bleaching and souring liquors is also sometimes effected, as above, in the washing machine (which in connection with such operations will be referred to as the chemicking or souring machine respectively), when the cloth is too heavy or closely woven to permit of ready penetration of the liquor by mere gravitational circulation, or it may be adopted in conjunction with circulation as an auxiliary treatment Otherwise the cloth is plaited down on a stillage to allow the liquor to complete the action which is only commenced in the machine During the passage of the cloth through the machine the liquor in the box must be maintained at a normal strength by the supply of a constant trickle of concentrated liquor to compensate for the dilution (effected by the moisture brought in with the cloth) and extraction of liquor during its passage, an operation *which is obviously somewhat difficult to regulate with accuracy*

A special instance in which souring is always carried out in the machine is the process which follows the wash out of lime boil, the object of which is to decompose the insoluble lime soaps produced in the lime boil, dissolve out any residue of lime or other earthy substances present, and assist in the loosening of the colouring matters This process, occurring early in the routine, while the cloth would still offer considerable resistance to ordinary circulation, admits of thorough penetration and affords the best means for carrying the above operations into effect

In all other processes than the above mentioned and that of washing, the cloth is normally treated by the boiling, bleaching, and souring liquors *in situ*, and the motion is imparted to the liquor by various means of circulation, though, as indicated later, a certain degree of motion is incidentally imparted to the cloth

There are also exceptional cases in the treatment of cloth, even in the rope form, *in which it is neither boiled nor bleached in a stationary condition*, but run through the kier or caused to traverse through the liquor, as described later. In all the stationary processes the first consideration is to get uniform percolation of the liquor through the cloth This is of additional importance in the case of boiling, because uneven boiling means uneven bleaching, and the worst and most ineradicable defects are those which arise from ineffectual treatment of the cloth in the earliest and most resistant stages

Plaiting.—The first precaution favouring uniform circulation is the proper disposal of the cloth in the kier, etc This process of packing is termed "plaiting," and is the first step in a bleacher's education. The cloth is fed into the kier after washing or impregnating, by means of an overhead wince, two ends being fed simultaneously, one to each half of the kier, and in its descent is guided by the plaiter (using a short staff for the purpose) into a series of laps, with which he forms a uniform layer, conforming the same to the semicircular shape of his half of the kier, the same of course occurring in the other half and with cloth of a similar quality. This is repeated in successive layers, but with frequent changes in the direction of plaiting, so as to place laps in consecutive layers

crosswise, thus preventing entanglements and rendering uniform the obstruction offered by the cloth to the flow of liquor

The plaiter is meanwhile treading down the cloth into a compact mass, special clogs with clean flat soles and brass nails being worn for the purpose, or else clean rags being wrapped round the feet When a coloured heading (or distinguishing mark) occurs at the end of a piece, the machine minders signal the plaiter for its approach, and it is dealt with when it reaches him, as indicated in the section treating of coloured goods Plaiting is sometimes effected without trampling, and from the top of the kier, as in the case of chemicking and souring, when a spray of liquor is pumped on to the cloth during its entry into the tank, or at the commencement of a boiling process, when the boiling liquor is prepared and lies at the bottom of the kier

Various attempts have been made to perform the operation of plaiting by means of automatic mechanisms, but without much success as regards the packing of the cloth for boiling bleaching, or souring Examples of successful devices in connection with piling on stillages, whiteboxes, etc , have been developed, as in the case of the Edmeston Bentz system It is also customary to effect the delivery of cloth in the open width from scutchers, mangles, etc , in laps or folds, by the employment of a mechanical plaiting device, which imparts a wave like motion to the descending cloth, whereby it disposes itself in a series of folds as it reaches the receptacle into which it is being fed Such a device is seen in the lower portion of fig 100, and in other illustrations

A special method of arranging the folds of cloth in the rope form, in a kier, is described in connection with the Thies-Herzig system (fig 110), in which the cloth is fed through a tube, the delivering end of which is guided in a systematic manner within the kier during packing, and as the cloth emerges from this tube, it disposes itself into a series of vertical folds, as indicated thus

A similar principle is involved in Eng Pat 136713, 20th February 1919 The goods are fed in rope form, together with the lye, through a hollow trunk of metal into the kier The trunk is hinged and pivoted to a metal box casting and receives a reciprocating motion lengthwise to the kier, and also a transverse oscillating motion The speed may be varied at will Thorough impregnation and regular packing are thus ensured In Eng Pat 137947, 5th March 1919, a hollow plaiting arm is used with rollers at the end

CHAPTER XVII.

ALKALI BOILING—GENERAL CONSIDERATIONS.

THE goods are now ready for the next process, viz. the lye boil or bowking operation, which is the most important of all It may be said, without reservation, that good lye boiling is the foundation of successful bleaching Faults of omission or commission made in this process cannot be rectified subsequently, except by repeating the whole operation from the beginning No effort should be spared to make the lye boiling complete. Badly boiled or incompletely "bottomed" cotton is not only a source of trouble to the bleacher, making the subsequent processes more difficult, but is a frequent cause of complaints and claims for damages The lye boil consists, briefly, of boiling the cotton with a solution of an alkali in order to change the impurities other than the natural colouring matters into soluble compounds which can be washed away by means of water. These changes are—

1 Saponifiable oils and waxes are converted into soaps.
2 Proteins are hydrolysed into soluble degradation products
3. Simpler amino compounds are dissolved or hydrolysed to ammonia
4 Pectose and pectin are changed into soluble salts of pectic or metapectic acid
5. Mineral matter is dissolved.
6 Unsaponifiable oil is emulsified by the soluble soaps formed from the saponifiable oils
7. Dirt forms colloidal adsorption compounds with the soap, or is removed mechanically by the process of pedesis
8 Dressing and sizing materials, such as starch or glue, are changed into soluble compounds.

The boiling process is carried out in specially constructed vessels termed kiers. These may be either open or loosely covered, in which case the liquor boils at atmospheric pressure, or closed, like a Papin digester, when the liquor boils at a temperature corresponding with the steam pressure

Only dilute solutions of alkalis can be used These saponify fats very slowly when boiled at atmospheric pressure. At temperatures above 100° C. the rate of saponification is much greater. Hence closed kiers in which the temperature can be raised are generally used. The heating is accomplished, as a rule, by steam pipes or by live steam, and some mechanical and automatic method for maintaining circulation of the boiling liquor is always provided.

Kiers will be described fully in the following chapter.

Two systems of lye boiling are in general use, viz. (*a*) the lime boiling and (*b*) the soda boiling.

The former, or "lime boil," is the older. It is used chiefly in the Lancashire trade, and particularly for heavy goods. The latter, or "soda boil," is

used for fine goods, such as nets, curtains, and yarns. The lime boil consists of several distinct processes. The goods are impregnated with milk of lime and packed in a kier, which is then filled with milk of lime After expelling all the air the lid is screwed down and the lye is heated for some hours at a pressure of about 20 lbs. This converts saponifiable oils and waxes into insoluble calcium soaps, pectoses and pectins are hydrolysed to pectic acid, which then forms insoluble calcium pectate, proteins and amino compounds are hydrolysed and dissolved, while tannic acid, if present, would be converted into insoluble calcium tannate. Mineral impurities are not affected much. After boiling, the goods are washed well with water to remove all the soluble constituents. They are then soaked in dilute sulphuric or hydrochloric acid of about 2° Tw. strength This decomposes the calcium soaps and pectates, giving soluble calcium sulphate or chloride, while the free fatty and pectic acids are left on the fabrics If calcium tannate were present, the tannic acid formed by its decomposition would pass into solution. The excess of acid, together with the soluble products of its action, are now washed away with water. The washed goods are then boiled again, but this time with a solution of sodium carbonate Some rosin soap is generally added also Both fatty acids and pectic acid are readily dissolved by a hot solution of sodium carbonate, and can now be removed by washing with hot water The milk of lime is made by grinding lime (56 lbs) with water (100 gallons) and passing the mixture through a fine sieve The rosin soap is made as required, by boiling rosin (10 lbs) with either sodium hydroxide or sodium carbonate (35 lbs) and diluting the solution of rosin soap produced with about eight times its volume of water

In the soda boil the goods are impregnated with a dilute solution of sodium hydroxide (approximately 2 per cent) and packed in the kier Sufficient of the sodium-hydroxide solution is added to cover the goods. After expelling the air, the lid of the kier is screwed down and the liquor is heated for some hours to a temperature of about 120° to 130° C. In this case the saponifiable oils are converted into soluble soap, the pectins into soluble sodium metapectate, the proteins and amino compounds into soluble degradation products, much of the mineral matter is also dissolved In fact, all the impurities other than the natural colouring matters are rendered soluble, and can be removed completely by the thorough washing with water which follows the boiling.

The lime process, as stated above, is used chiefly in the Lancashire district, and, in particular, for the "full white" or "madder" bleach, when the most thorough bottoming together with avoidance of overbleaching is demanded. The soda process is more suitable for fine goods which might be mechanically damaged by the milk of lime It is also simpler to carry out, involving fewer processes Except in the cases named it is gradually replacing the lime-boiling process.

The relative merits of the two methods have been the subject of much discussion, and the definite superiority of either is not conclusively established. It is not clear wherein the advantages of the lime boil lie, having regard to the extra processes involved But many experienced bleachers are convinced of its superiority, in fact, this belief is one of the most interesting features of the Lancashire trade Among the advantages claimed is that the goods do not come into contact with sodium hydroxide, and hence the danger of mercerisation and shrinkage is avoided. Calcium hydroxide does not produce these effects. Moreover, the presence of calcium hydroxide is said to protect cotton from mercerisation. For example, in the Thies-Herzig process the cotton is first impregnated with a solution of calcium or magnesium chloride. It is then

boiled with sodium hydroxide. It is claimed that strong solutions of caustic soda may be employed without causing shrinkage or mercerisation. The first action of the sodium hydroxide is to precipitate calcium or magnesium hydroxide in the goods—

$$MgCl_2+2NaOH=Mg(OH)_2+2NaCl.$$

According to Georgevics (*Chemical Technology of Textile Fibres*, p. 69), the goods are first steeped in a "sour" containing 1 per cent of 60 per cent sulphuric acid, or 1·6 per cent. of 30 per cent. hydrochloric acid, together with 0·005 per cent of 75 per cent. hydrofluoric acid. The reaction is accelerated by warming the bath or by steaming the goods, when they leave the cold bath, for thirty seconds After washing, the goods are steeped overnight in a 0·5 per cent solution of sodium hydroxide. They are then passed into a 0·005 per cent. solution of magnesium chloride, and then through a wringer into the kier, where they are boiled with a 5 to 7 per cent solution of sodium hydroxide. The solubility of magnesium hydroxide in water is about 1 in 50,000 A later development of this process has been noted under "Plaiting," and will be referred to again in connection with kiers

This process, although of interest in itself, can hardly be regarded as evidence in favour of the lime boil, since if the souring process be carried out properly no calcium nor magnesium salts are present in the washed cotton Further, calcium or magnesium salts would be converted into insoluble carbonates when brought into contact with sodium carbonate. That the likelihood of mercerisation and shrinkage is small in the lime-boiling process is due entirely to the fact that sodium carbonate is used after souring If this contains sodium hydroxide as an impurity the advantage disappears On the other hand, if dilute solutions of sodium hydroxide are used intelligently, the shrinkage produced is very small. Excessive shrinkage and local mercerisation does often occur, but, generally, as the result of unintelligent methods An example may be given. Excessive shrinkage and local mercerisation, accompanied by distortion of pattern, were traced by the author in one case to be due to the following cause. A few bucketfuls of concentrated caustic soda solution of mercerising strength were put into the bottom of the kier The goods were then packed and the kier filled up with water. When the boiling commenced, the concentrated sodium-hydroxide solution was ejected by the puffer pipe on to the goods before it became diluted Immediate shrinkage and mercerisation occurred. When proper precautions were taken to prevent this concentrated alkali from coming into contact with the goods the trouble ceased

Many bleachers think that they can get a better finish on goods that have been boiled with lime than on those treated with sodium hydroxide. This again is rather an assumption, being only true when a harsh feel is not only no objection, but is actually desired It is claimed that the lime boil removes the cotton waxes more completely than the soda boil. Thus Higgins (*Bleaching*, p. 40) says. "Lime boiling is not a mere survival of the days of empiricism; it is the best treatment for some classes of goods, for the figures given above show that it is the best means of removing waxes from the fibre." The figures referred to were obtained from experiments by Higgins on linen cloth and yarn. When boiled with lime the residual wax was 0·046 per cent., while with sodium hydroxide it reached 0·16 per cent. The supposed superiority of the lime boil is due to the fact that after the sour the free fatty acids and unsaponifiable matter are intimately mixed on the fibre. When these come into contact with sodium carbonate, saponification of the former and emulsification of the latter

take place both rapidly and completely On the other hand, the complete bottoming which can be obtained by a properly conducted soda boil is indisputable The author has examined many samples of soda-boiled goods which contained only traces of either fat or nitrogen, and less than 0·05 per cent of mineral matter A number of experiments showed that in every case the loss of impurities due to lime boiling was less than that caused by soda, even when hydrochloric acid was used for decomposing the lime soaps When sulphuric acid was used the lime left in the fabric was very considerable, amounting in many cases to as much as 0 52 per cent This is partly present as lime soap, partly as carbonate and unremoved sulphate The following table gives the results of some parallel tests made on the same cottons The figures represent percentages found in the cotton after boiling

	Experiment 1.		Experiment 2		Experiment 3	
	Soda Boil	Lime Boil	Soda Boil	Lime Boil	Soda Boil	Lime Boil
Ash .	0 26	0 72	0 26	0 50	0 42	0 56
Free fat .	0 10	0 26	0 20	0 1	0 16	0 11
Fatty acids as soap	0 16	0 22	0 13	0 21	0 26	0 56
Nitrogen .	0 05	0 70			0 07	0 07

The saponifying power of calcium hydroxide is rather remarkable At first sight it would seem that since the calcium and magnesium soaps are insoluble in water saponification would proceed very slowly, but, as a matter of fact, this is not the case The same thing has been observed in the case of limed skins in which it is found that saponification takes place at ordinary atmospheric temperatures

The advocates of the lime boil hold that the preliminary impregnation of the goods with milk of lime favours the setting up of a number of centres of chemical activity But opposed to this view is the fact that strontium hydroxide, which is more soluble than calcium hydroxide, saponifies fat more readily, in fact, saponification must proceed more rapidly when the saponifying agent is completely soluble, like sodium hydroxide Weiss (*J S C I*, 1919, 715A) states that strontia saponifies oils three times as quickly as lime, and gives a better colour to the goods He suggests using a liquor containing 20 grammes of strontium hydroxide, $Sr(OH)_2 8H_2O$, per litre, or a mixture of strontium and sodium hydroxides

The danger of producing oxycellulose is not lessened by the use of lime In fact complaints of tendering are more common than where the soda boil is used These are, however, due partly to local burning owing to careless slaking or the use of unsuitable lime If any incompletely slaked particles become entangled in the goods they commonly cause trouble Lime which contains magnesia slakes very slowly, and in such cases unslaked particles may pass through the sieve

The lime-boiling process is said to cost less than the soda boiling, but with regard to this, the additional coal and labour must not be overlooked Moreover, the soda process is certainly quicker, and the question of time is often an important one Goods are sometimes received on one day, and must be bleached and delivered on the next In such cases the use of the lime-boiling process would be out of the question

Again, for all cotton materials which from their nature present difficulty in handling or mechanical washing, the shorter process is always better, while such goods as cops, cheeses, warps, loose cotton, sliver, etc, present the greatest difficulty to impregnation or boiling with lime

The use of rosin in the soda ash or sodium-carbonate boil is an essential part of the lime process Rosin soaps, as elsewhere indicated, have very marked lathering and detergent properties, but their use demands very thorough washing with soft water, if good colour is to result in the finished goods In the opinion of the author the use of rosin in any form is objectionable in the case of fine goods, or those requiring a perfect white

The effects produced by hard water in conjunction with rosin soaps have already been referred to (*vide* Chapter XI, p 197). With hard water it is almost impossible to completely remove these soaps, and very small quantities of calcium or magnesium resinates will deleteriously affect the colour of fine cotton goods Experiments made by the author and others have proved that, even with distilled water, it is difficult to remove rosin soaps completely A series of tests made under identical conditions proved conclusively that in no case was the colour so good when rosin was used (Trotman, *J S C I*, 1905, p 267)

Jackson (Cantor Lecture, 1907) confirms these results He made a large number of tests under strictly comparable conditions with many soaps free from rosin, and with soaps similar in other respects, but containing varying properties of rosin He found that goods washed with the latter became coloured When the washing was repeated the colour gradually increased, and it was not a matter of opinion, but an indisputable fact The difference was quite noticeable even when the rosin did not exceed 5 per cent of the total acids in the soap, and the higher the percentage the more marked was the effect In this lecture he was speaking mainly to launderers, but his experience coincides with that of the author and other observers

In connection with the ash boil used in the lime process the use of "assistants" is very common These are used under various names, cresolate of soda being very common They are supposed to assist the ash in its work These bodies are generally employed without any exact knowledge of their composition, and many of them are simply disguised soda or carbonate of sodium The following analysis of a "soap substitute" illustrates this point —

Sodium carbonate	25 75
Sodium silicate	2 50
Soap	1 50
Neutral salts	76 25

In general, it may be regarded as undesirable to make use of assistants whose composition and method of action are unknown Readily saponifiable oils, such as castor oil, are employed also, and are often useful By the formation of soap they assist both penetration and emulsification, and are thought to protect the fibre from access of oxygen Sulphonated oils, such as turkey red oil, are still more effective than castor oil

Well boiled cotton should contain only mere traces of nitrogen, not more than 0 10 per cent of fatty matter, including wax, and but little mineral matter There is no difficulty in removing the nitrogenous impurities Higgins has shown that in the case of cotton either type of lye boil should remove protein nitrogen completely, the unremoved residue being associated with the colouring matter Knecht and Hall (*J Soc Dyers and Col*, 1918, p 220) state that the soda boil removes 80 per cent of the total nitrogen, and that after bleaching and

souring 5·8 per cent of the total nitrogen still remained Higgins (*J Soc Dyers and Col*, 1919, p 165) agrees, but says that this cannot be protein nitrogen, since it does not give the chloramine reaction There is more difficulty in the case of oil and wax Hebden (*J Ind. Eng. Chem*, 1914, p 714) found that 64 per cent of the total was removed during soda boiling Knecht, Higgins, and others have also shown that neither process removes these bodies completely This point will be referred to again The pectoses and pectins should be removed completely, and over 90 per cent of the mineral matter also

The importance of the lye boil being so great, it is very necessary to understand something of the factors which determine its success

The conditions necessary to ensure a satisfactory boil are—

1 The use of suitable water
2 Good packing and circulation in the kier
3 Absence of air and oxygen
4 The presence of sufficient alkali
5 The complete removal of the lye immediately after the boil and thorough washing of the boiled goods
6 The absence of direct contact of the goods with steam pipes
7. Purity of the reagents used.
8 Cleanliness of the kier

Water used in Lye Boil.—This should be as soft as possible If hard water be used, it will, in the presence of sodium hydrate, form lime and magnesia. These will in turn fix their equivalent of fatty acids as insoluble soaps in the fabrics, and the latter can only be removed by decomposition with acid The damage caused by lime and magnesia soaps has already been referred to (Chapter XI)

The following is a concrete example Two equal quantities of cotton were boiled with caustic soda solution, the solution being in one case made with distilled water, and in the other with water containing 40 parts of hardness per 100,000 At the end of four hours the fat removed was estimated The results showed that in the first case 23 per cent more of the total fat had been removed Goods bleached with hard water can always be detected by estimating the fat and soaking in acid, washing, drying, and extracting the free fatty acids. It is by no means uncommon to find as much as 0·3 to 0·5 per cent. of fatty acids as soaps There is no doubt that soft water is far better than merely softened water, since many neutral salts, such as sodium chloride and sulphate, if present in any quantity, have a retarding effect on saponification. This point will be returned to again later

Freedom from iron should be ensured both in the original water and condensed steam, where this is used Very small quantities of iron are sufficient to cause loss of pure colour. It has been proved that discoloration may be caused by as little as 0·05 grain per gallon

The importance of circulation has already been referred to In the soda boil it can hardly be overestimated Experiments have shown that the rate of saponification of oil by means of caustic alkali depends very greatly upon the velocity of circulation The lye tends to become weakened in contact with the goods, and, if the circulation be faulty, it is not rapidly replaced by fresh liquor The effect of this is that, after a time, the rate of saponification diminishes and the goods are incompletely scoured. Most kiers contain some form of apparatus for ensuring continuous circulation. Among these are spreaders or puffer pipes,

injectors, centrifugal pumps, the use of a vacuum, etc. These will be referred to again when dealing with kiers.

Packing of Goods in the Kier.—The method of packing has been fully described The goods should be so arranged that spaces in which steam or air could collect cannot be formed between the layers, since this is a frequent cause of overheating and causes mechanical stress sufficient to break fine goods. The closer the goods are packed, the less likely this is to happen; but close packing emphasises the importance of good circulation. If the packing be uneven the liquor will tend to circulate freely through the loosely packed portions, following the line of least resistance and leaving the tightly packed goods, which offer greater resistance The saturation of the goods previous to plaiting has already been described. Care must be taken that the goods are completely immersed in the soda solution and that no steam pipes come in contact with them. Neglect of these precautions causes incomplete scouring or local damage from burning.

Absence of Oxygen.—This is perhaps the most essential condition for good soda boiling. We have already seen that although dilute alkaline solutions have no action on celluloses in the absence of air, they readily attack them in the presence of oxygen, forming oxycellulose The formation of oxycellulose means destruction of tissue and consequent tendering Moreover, a fabric containing oxycellulose often develops a brownish tinge on keeping Air is sometimes present owing to bad packing or imperfect impregnation of the goods The tendency to oxidation is perhaps increased by the power which cotton has of absorbing gases. Bowman states that it is capable of occluding seven times its volume of oxygen. Air not only causes oxidation, but, expanding on heating, produces air-bubbles, which protect the cloth from the action of the lye

The most usual method of getting rid of air in a boiling kier is to keep the air or safety valve open for a short time after commencement of the process, or, when sufficient steam is up, to create a slight pressure, to observe the colour of the jet which issues from the outlet pipe When air is coming out with the steam the gust acquires a blue tinge, and when this ceases the valve may be closed Another method is to enter the liquor from below the cloth, thereby carrying upwards bubbles of air imprisoned in the cloth Considerable damage and loss have been incurred in many works employing the low-pressure lime boil through nothing but access of air to the cloth when there is an insufficiency of liquor, or when the cloth rises up in the kier and becomes exposed to the air. Such damage is always most apparent at the sides and top, but the flow of liquor, when the top of the cloth is not flooded, appears to draw down into the cloth a quantity of air which attacks a considerable number of layers

The most effective remedy is of course to have sufficient liquor to start with which is difficult in view of the subsequent condensation of steam But even then it is better to lose some liquor later on by overflowing and start with plenty, even at the cost of the extra lime employed. The cloth should be well weighted to prevent its floating, and the sides and top covered with sheets The aeration of the discharge from the puffer pipe may be diminished by putting a sack over it, but this device is also employed to direct the discharge towards the centre of the kier when required, and to prevent splashing, and must not be made use of to the extent of robbing the outer area of liquor. A light cover spanning the top of the kier is a good safeguard against air, as the space enclosed is then filled with steam. All these troubles are avoided in the pressure kier.

In connection with the foregoing remarks about the danger caused by access of oxygen, it is interesting to note that in one system of soda boiling, the piling of soda-saturated goods overnight is actually recommended, stress being laid on

the fact that bleaching action proceeds during the night Of course the danger of forming oxycellulose is minimised by the low temperature, but the tensional effects referred to cannot be absent It would be a good practice to de-aerate the water used for lye boiling by means of a little sodium hydrosulphate

Removal of Lye in the Absence of Air.—After the boiling, the hot lye should be run off and the goods should be washed, so far as is possible, in the kier, and not exposed to the action of the air until they are nearly free from alkali and thoroughly cooled The incomplete removal of soda before the goods are removed favours, of course, the production of oxycellulose ; but it is also objectionable for another reason. If cotton be left exposed to the air, in contact with a weak solution of caustic soda, this will gradually become concentrated by evaporation, especially if the solution was hot at the start In this way the lye will ultimately reach the concentration necessary to exercise a mercerising effect Mercerisation is accompanied by shrinkage In the case of goods, like lace curtains, containing a tightly made pattern, these patterns, being unyielding, offer a considerable resistance to the shrinkage, and thus tension results The bobbin threads being much finer than the remainder are often unable to withstand this tension, and consequently break Even if they do not break, considerable distortion of pattern often results This may be caused by lifting the lid of the kier, and leaving the goods exposed to get partially dry, instead of washing at once (*vide* Trotman and Pentecost, *J S C I*, 1910, p 4)

Mercerisation caused by introducing concentrated lye into the bottom of the kier has been referred to on p 285 Thorough washing is not only necessary to completely remove the lye, but to carry away all traces of impurities rendered soluble by the boiling In the absence of thorough washing some of these will be left in the fibre and become re-precipitated as fatty acids, pectic acid or protein in the later processes The results thus produced are indistinguishable from those of an imperfect boil Owing to the tenacity with which sodium hydroxide clings to cotton, it is, however, quite sufficient to wash until the cotton has no longer an alkaline reaction

After completion of the boil the goods should never be allowed to cool off in the lye Higgins (*J Soc Dyers and Col*, 1912, p 151) showed that during cooling some of the impurities removed by the hot lye were reabsorbed by the cotton

Presence of sufficient Alkali.— Although the concentration of the soda solution may vary between certain limits, it should be regular in composition Too weak a solution will prolong the time necessary for a complete boil, and if too strong it may cause undue shrinkage It may be remarked in this connection that the practice of determining its strength by means of a hydrometer is extremely crude and fallacious. The hydrometer value assumes that everything in solution is soda, or that the impurities are always constant in quality and quantity Caustic soda, as we shall see later, is liable to variation in strength and to contain carbonate of soda and other impurities, none of which can be indicated or measured by the hydrometer

The estimation of caustic soda and carbonate by means of a standard acid solution does not occupy much more time than the use of a hydrometer, and gives results upon which reliance may be placed.

In using a hydrometer the liquor must first be brought to a temperature of 15° C , for which the instrument is graduated Either the Baumé or Twaddell hydrometer may be used. The relation between the readings of these is given later.

In addition to the quantity of alkali in the lye, it is necessary to have a

sufficient volume present to completely cover the goods and saponify or render soluble all the grease, albuminoids, etc The quantity varies according to the process used and the effect desired, but it is generally between 2 and 5 per cent of the weight of the fabrics It must always be sufficient in volume to admit of adequate circulation through and complete saturation of the goods Any quantity used in excess of these requirements entails waste of chemicals, unless the lyes are collected and used again a course of action generally to be avoided.

The necessary quantity having been weighed, it is dissolved in water sufficient to make the lye of the desired concentration and to completely cover the goods to be treated According to Taylfer, the proportion of 60 gallons of lye for each 100 lbs of goods should not be widely departed from

The solution of caustic soda or potash in water presents some difficulty, as it is apt to cake if simply dropped into water, and it then dissolves only very slowly The best plan is to suspend it in the water in a cage of wire gauze which is sufficiently fine to prevent the solid from escaping It can also be dissolved in a small quantity of hot water with stirring, and afterwards diluted. Both caustic soda and potash contain a good many insoluble impurities which either rise to the surface or settle according to the specific gravity of the solution These should be removed before use This is readily done if the soda solution is always prepared in a separate vessel or tank

The volume of liquor to be originally introduced to effect suitable concentration depends also upon the accession of condensed steam which occurs during the process, when the heating or circulation is effected by live steam Not only does this steam condense and decrease the strength of the liquor, but it may also impair the efficiency of the circulation, causing the goods to float and even protrude from the kier For this reason, when steam pressure is low and the ratio of volume of steam to heat content is high, the bleacher is tempted to commence operations with a volume of liquor which is insufficient to produce thorough circulation and saturation until a sufficient quantity of condensed steam has accumulated, so that he may not be embarrassed by too great a volume of liquor at a later stage

Temperature of Lye Boiling.— The rate of saponification depends not only on the circulation in the kier, but also upon the temperature In open kiers the temperature can never be above the boiling-point of the lye employed, which will be approximately 100° C By boiling in closed kiers under pressure the temperature is correspondingly increased and the time necessary for saponification and solution of the albuminoids decreased. The temperature employed varies from 100° to 130° C The pressures corresponding to these temperatures are given in the following table —

Pressure in Atmospheres	Temperature of Steam
1 00	100 00° C
1 25	106 33° C
1 50	111 33° C.
1 75	116 50° C
2 00	120 64° C
2 25	124 39° C.
2 50	127 33° C
2 75	130 98° C

130° C. may be considered as the maximum temperature which cotton will safely stand. If heated above this point, it gradually becomes brown in colour owing to incipient decomposition.

The Purity of the Reagents used.—This is a factor which exercises a greater effect than is generally recognised. Although caustic soda and sodium carbonate are readily obtained in a state of approximate purity, yet they sometimes contain distinct quantities of chlorides and sulphates, of alumina and iron One comes in contact with so many cases of incomplete boiling where apparently the conditions have been favourable, that one is sometimes forced to the conclusion that some bodies must have been present which exercise an inhibiting effect on the saponification of fat and the solution of proteids and pectins Certain effects of neutral salts have already been mentioned in connection with water and water softening. The following experiments (Trotman, *J S.C I*, 1910, p 249) show the retarding action which they have on the soda boil. A constant dry weight of cotton was boiled with a definite volume of 2 per cent pure caustic soda under an inverted condenser with and without the addition of the neutral salt The cotton was then thoroughly washed with distilled water, dried and weighed, and the percentage loss determined The same cotton and soda solution were used for each set of experiments. The following results were obtained, the figures representing percentage loss on the dry weight –

Effect of Sodium Chloride

	Percentage Loss
Cotton and pure caustic soda	4 47
,, caustic soda containing 0 13 per cent sodium chloride	4 08
,, ,, ,, 0 30 ,, ,, ,,	3 98

Many lyes contain more than this amount of sodium chloride

Effect of Sodium Sulphate

Cotton and pure caustic soda	6 75
,, caustic soda containing 0 146 per cent Na_2SO_4	6 33
,, ,, ,, 0 292 ,, ,,	6 14
,, ,, ,, 0 338 ,, ,,	5 95
,, ,, ,, 0 584 ,, ,,	5 85
,, ,, ,, 0 730 ,, ,,	5 76

In this case the residual fat and nitrogen were determined with, and without, the addition of sodium sulphate, and were found, as was expected, to be greater when sodium sulphate was present.

Effect of Alumina.

	Percentage Loss
Cotton and pure caustic soda	5 20
,, caustic soda containing 0 035 per cent Al_2O_3	5 15
,, ,, ,, 0 070 ,, ,,	5 09
,, ,, ,, 0 175 ,, ,,	4 63

These results tend to show that very small quantities of alumina are sufficient to retard the action of the soda A second set of experiments made with potash alum gave still more marked results—

	Percentage Loss.
Cotton and pure caustic soda	5 00
,, caustic soda containing 0 166 per cent. crystalline alum	4 88
,, ,, ,, 0 332 ,, ,, ,,	4 25
,, ,, ,, 0 498 ,, ,, ,,	4 06

Effect of Iron.—The effect of iron was even more marked than that of alumina—

	Percentage Loss
Cotton and pure caustic soda . . .	5 38
„ caustic soda containing 0 0057 per cent Fe	4 74

Effect of Zinc Sulphate.—Zinc compounds are often used as antiseptics or for weighting, and hence are often present in the lye

	Percentage Loss.
Cotton and pure caustic soda	5 20
„ caustic soda containing 0 033 per cent $ZnSO_4 7H_2O$	4 99
„ „ „ 0 066 „ „	4 86

Effect of Calcium Sulphate

Cotton and pure caustic soda .	4 54
„ caustic soda containing 0·049 per cent $CaSO_4$	4 32
„ „ „ 0 06 „ „	4 17
„ „ „ 0 08 „ „	3 84
„ „ „ 0 10 „ „	3 66

It is evident from these results that in the absence of neutral salts the time necessary for a complete boil is considerably shortened These experiments seem to show that hydrochloric acid should always be used for souring after the lime boil owing to the greater solubility of calcium chloride

The importance of the use of the best materials is also emphasised by Cross and Bevan (*J S C I.*, 1889, p 252), who conclude that wherever caustic soda is used in the arts as a hydrolytic agent the maximum of chemical work is obtained, *ceteris paribus*, with the minimum of impurity in the reagent.

The relative efficiency of pure and impure (commercial 60 per cent) caustic soda was tested by experiments upon esparto Equivalent quantities were used under exactly similar conditions The pulp obtained from the pure soda contained 88 per cent of cellulose, while that from the 66 per cent. soda gave only 77 per cent The external characters of the pulps and their behaviour on bleaching corresponded with the difference thus proved in favour of the former.

The effects of neutral salts were also investigated with esparto The addition of sodium chloride and sulphate was found to cause a considerable deterioration in the quality of the pulp The composition of the 60 per cent soda used was

NaOH	71 08
Na_2CO_3	8 22
NaCl .	8 47
Na_2SO_4	2 38
Na_2SO_3	3 34
Al_2O_3 .	2 78
Fe_2O_3 .	0 18

If this product be bought at the same price, *pro rata*, as the pure product, it shows a considerable percentage "discount of value" in view of the above facts.

The sample, according to Cross and Bevan, would show by the ordinary alkali test about 61·66 per cent. of alkali. It only contained 60·72, giving a difference of 0·94 per cent. Since carbonate of soda only has about half of the chemical activity of sodium hydrate, a further reduction of 2·40 per cent must be made. To this must be added the retarding action of the salts and alumina. To counteract the whole of these impurities, at least 5 per cent. more alkali will be required. Thus we have a total loss of 8·24 per cent.

Higgins (*Bleaching*, p 31), referring to these facts, says. "These observations point to the importance of washing the cloth well after a sour steep, and also indicate the advantage of using pure chemicals By means of steeping before scouring many of the impurities of the grey material, which are now known to affect the boiling process, are removed, and, perhaps, for the first time we have an explanation of the fact that the steep is found advantageous in so many cases" Starch is also known to have a retarding effect upon the action of the lye boil

Absence of direct Contact of the Goods with the Steam Pipes.—In all well-constructed kiers this is provided against The goods frequently become burnt through direct contact with such pipes

Cleanliness of the Kier.—This is as important as cleanliness in the other processes. The sides should be frequently scraped, washed, and lime washed In kiers used for lime boiling, the deposit of lime must not be allowed to accumulate on the walls to the extent of causing rough projections which would fray the goods as they move up and down This is probably a cause of "shot-holes," though these are variously ascribed to the action of steam attacking the cloth through the false bottom, and to bad circulation due to hard places caused by irregular plaiting As the identical effect has been discovered on cloth that had passed through a mangle in which one of the bowls had a transverse motion owing to worn pedestal necks, the friction theory is at least plausible Meanwhile, shot-holes remain a menace, and are an inducement to attend to rough deposits in the kier The reduction of lime deposits is assisted by alternating the lime and soda ash boils in the same kier

Completeness of Boil.—If from any of the causes indicated above, whether too weak a lye, insufficient time or circulation, or deposition of soaps, the goods are not thoroughly bottomed, the remaining operations are bound to be unsuccessful The whole object of the boil is to render soluble and remove the greases and waxes, albuminoids, etc Not only does bleaching powder not touch these, but their presence protects the cotton from its action, and in some cases they form actively deleterious compounds with chlorine or hypochlorites Thus, if the wax be not completely saponified, it remains as an impenetrable coating on the fibre and protects the colouring matters from the action of the chemic

The same remarks apply to unsaponifiable oils, such as paraffin or lubricating oil, in a still greater degree These are in any case very difficult to remove, an emulsification by means of soap and carbonate of soda being the only method available The use of organic solvents is, of course, theoretically excellent, but in practice rarely employed

If the proteins are not thoroughly removed from cotton during the soda boil, as soon as the goods come into contact with the bleach they absorb chlorine, with the formation of these chloramine compounds These may become subsequently decomposed with liberation of hydrochloric acid and tendering will result, or the gradual decomposition may cause fading in stained or coloured goods

Further, an incomplete boil may leave tannic acid, which, in presence of iron, immediately produces tannate of iron, which has a characteristic black or blue-black colour Cotton goods after bleaching sometimes develop blue or black discolorations from the converse reason. That is, they may contain iron and be allowed to lie on a wooden table which contains tannic or gallic acid, the presence of these acids being rendered visible by the development of blue or black stains or spots

If the above conditions have been carefully observed, all the impurities other than certain colouring principles will either have been removed or rendered soluble and removable by a thorough washing with water. The cotton will then be ready for the chemic.

Use of Caustic Potash instead of Soda —Potash soaps are more soluble in water than the soda compounds, and a potash soap will scour cotton more rapidly than a soda soap In the same way, caustic potash is more efficient than caustic soda for the lye boil It saponifies more rapidly, and the resulting soaps are more readily removed. A large number of experiments made in the author's laboratory proved that in a given time caustic potash removed from cotton about 1 per cent more than caustic soda Its use is more expensive, but it is to be recommended in many cases where goods are difficult to bottom, or time is pressing.

Other Bodies used in Lye Boiling.—Other alkaline compounds are also used either with, or without, caustic alkalis, the chief of which are sodium carbonate, sodium silicate, sulphide and sulphite, sodium borate or borax, rosin and other soaps Sodium carbonate has already been referred to; its chief use in the soda boil is as an emulsifier, and the same may be said of borax. Neither has any detrimental effect on cotton Sodium silicate has considerable scouring properties, but its use is not advisable with fine goods owing to the possibility of silica being deposited and mechanically damaging the goods Borax, like sodium carbonate, has little direct saponifying power, but possesses considerable detergent and emulsifying properties It is sometimes found in soap powders. As is to be expected, none of these bodies removes from cotton so much as caustic alkali, as is seen by the following table of results obtained with the same cotton —

Caustic potash removed	5 00
,, soda	4 40
Sodium carbonate	3 70
,, borate	2 80
,, silicate	2 40

Alkaline sulphides are sometimes used with coloured goods and are very effective They are, however, dangerous owing to their power of attacking metals and forming sulphides, which are generally black Metal surfaces are therefore rapidly attacked, and discoloration of the goods sometimes occurs. Further, chlorine and sulphides react very readily when brought into contact, giving rise to a chloride and sulphur—

$$Cl_2+H_2S=2HCl+S$$

Thus where sodium or other sulphide has been used in the boil the greatest care must be taken with the washing, if the goods are afterwards to be chemicked.

Sodium sulphite or bisulphite may be used with less danger, but both of these compounds are antichlors, *i e.* they are oxidised by chlorine, reducing it at the same time to hydrochloric acid. Thus, if goods containing sodium sulphite are put into chemic, sulphurous acid is first liberated, and this is then oxidised to sulphuric acid at the expense of the chlorine, as shown in the equations

$$Na_2SO_3+2HCl=2NaCl+H_2SO_3,$$
$$H_2SO_3+Cl_2+H_2O=2HCl+H_2SO_4.$$

In another process (Eng. Pat. 802, 12th January 1914) the cotton is digested under pressure with magnesium or sodium bisulphite containing excess of sulphur dioxide, the gases liberated being completely removed. It is said that no further

lye boiling is necessary, purification and bleaching being accomplished simultaneously.

Changes due to Scouring and Lye Boiling (Trotman and Pentecost, *J.S.C.I.*, 1910, p 4).—The changes due to scouring and lye boiling are—

1. Loss in weight
2. Loss in length
3. Alteration in count
4. Increase of tensile strength
5. Alteration in natural twist

Loss in Weight.—Very few attempts have been made to measure quantitatively the loss that may be expected when ordinary cotton yarn or goods are subjected to the soda boil This is to be wondered at considering how often, especially in the case of yarns, disputes arise as to the allowance to be made Although both parties to a dispute have their own ideas on the subject, they rarely base them on quantitative experiments, since neither, as a rule, knows the condition of the goods with respect to moisture before or after bleaching Thus a bleacher receives 100 lbs of cotton yarn containing x per cent. of water and delivers say 90 lbs of bleached yarn containing y per cent of water. The apparent loss is 10 lbs or 10 per cent, but the real loss can only be ascertained when x and y are known and allowed for Thus, if when received the yarn contained 92 per cent of dry yarn and 8 per cent of water, it must after bleaching be calculated to the same percentage composition before the loss can be found. The best way of doing this is, of course, to determine condition weight of the yarn before and after treatment The following numerical example will indicate the method to be adopted –

A parcel of yarn on receipt weighed 105 lbs A portion of it was weighed and dried and the percentage dry weight found to be 89 50

Thus we have

	Percentage dry weight	89 50
	Add regain 8½ per cent	7 61
..	Percentage condition weight	97 11

Weight of yarn containing correct amount of water on delivery $= \frac{105}{100} \times 97\ 11 = 101\ 96$

After bleaching the yarn weighed 95 lbs, thus showing an apparent loss of 10 lbs

A portion of the bleached yarn was tested as before and gave the following figures —

Percentage dry weight	92 00
Regain	7 82
Percentage condition weight	99 82

Hence the weight of true yarn in the bleached goods is

$$\frac{99\ 82}{100} \times 95 \text{ or } 94{\cdot}83 \text{ lbs.}$$

Therefore the true loss is 101·96—94·83, *i e.* 7·13 lbs, or 6·8 per cent.

The following table is a summary of a number of tests made with common

counts in this way, and since they have been made under strictly scientific conditions, should prove of some value :—

Reputed Count.	Percentage Loss	No. of Tests.
24/2 Am.	5 30	7
32/2 ,,	4 01	36
40/2 ,,	4·35	15
70/2 ,,	3 90	29
70/2 ,,	6·54	8
80/2 Eg	4·59	12
100/2 ,,	4·35	18
120/2 ,,	4 60	12
150/2 ,,	4 55	6

It is important to remember that goods must lose weight during the lye boiling if they are to be cleared from impurities In fact, the more weight they lose the more thorough has the process been If they lose but little weight they are very likely to become discoloured subsequently and give rise to complaints It was stated above that most of these complaints can be traced to incomplete lye boiling In the case of goods which are filled or weighted during finishing, loss of weight is of relatively little importance Higgins (*J Text Inst*, 1916, p 29) gives a number of examples drawn from large-scale experiments. In the case of cotton goods (damasks) the average loss in weight appears to be 9·75 per cent on the dry material

Loss in Length —The shrinkage due to boiling varies very much with the conditions. In the foregoing experiments the length of the yarn tested was measured before and after boiling, the average loss being 2·6 per cent

In commercial bleaching operations it is usual to allow 5 per cent for yarn which is not subjected to longitudinal tension, as is cloth in the rope, but this should not be reached

Alteration in Count - Since count depends jointly upon weight and length, it is obvious that it will be affected by both of the above losses. In speaking of an alteration in count, one must be careful to distinguish between the apparent count and the true count at correct condition with respect to moisture. The apparent alteration in count may be quite as misleading as the apparent loss in weight, for exactly the same reasons. The following table shows the results of a large number of tests of cotton yarns before and after lye boiling, in each case the " true " count being given .—

Count before Lye Boil.	Count after Lye Boil.
24	25·70
32	33 72
40	42·0
70	72·58
80	83 90
100	104·60
120	125·60
150	167·50

It will be noted, as might be expected, that the alteration gradually increases with the count.

Increase in Tensile Strength.—After a properly conducted lye boil, yarn will always show a greater breaking strength than before. Any weakening which might result from the removal of waxy matters is probably more than made up for by the thickening and felting of the fibres. Piece goods, such as lace curtains, are sometimes weaker after the boil because the finer threads have been unable to stand the strain caused by the shrinkage due to careless boiling As a general rule, any difference of breaking strength between unbleached and bleached yarn is due to the bleaching process and not to the soda boil

Alteration in Twist.—The mercerising effect of strong solution of caustic soda has already been mentioned, and it is always accompanied by a loss of natural twist, the fibres becoming in appearance more like tubes than twisted ribbons A certain amount of mercerisation and loss of natural twist always occurs during the soda boil This can be detected by the distinctly increased affinity for dyes which is now present The extent to which the change has taken place depends, of course, upon the method in which the boil has been conducted There is in addition an increase in the number of turns per inch given to a yarn due to the combined effect of shrinkage and tightening of the cotton

In a recent patent (Eng Pat 12086, 16th May 1914) it is proposed to protect cotton against shrinkage and damage during the lye boil by steeping it for from ten to twenty hours in water containing formaldehyde and a sulphonated oil It has been mentioned above that the former body protects cotton from mercerisation, the sulphonated oil being added, probably, to aid penetration

Hubner (*J Soc Dyers and Col*, 1922, p 29) found that the following process produces the greatest freedom of the scoured fabric from oils, fats, starches, and other ingredients used in sizing the warp with the least reduction in its strength.—

1 *Steep*.—Run the cloth into the open kier and boil lightly overnight with 1 per cent of soda ash

2 Run out of the kier, through rope washing machine, back into the kier.

3 *First Boil*.—Boil for about twelve and a half hours in the open kier with 1½ per cent of caustic soda and 1½ per cent. of soda ash

4 Run out of kier through rope washing machine

5 Sour with 1·50° Tw hydrochloric acid

6 Run through rope washing machine back into the kier

7 *Second Boil*.—Boil in the open kier, for about twelve and a half hours, with 3 per cent. of soda ash

8 Run through the rope washing machine until free from soda (generally four times)

9 Pass through water mangle.

10 Dry on the cylinders.

11. Impregnate with a solution of sodium acetate in the water mangle

12. Stenter and dry on clip stenter

13 Damp slightly

14. Plait and measure

The Use of Old Lyes.—The sodium hydroxide liquor drawn off from the kier is used, sometimes, as a preliminary "soak" for other goods. It may be recausticised also and used again in the kier This is done by boiling it with just enough milk of lime to decompose the dissolved soaps and convert the sodium carbonate present into sodium hydroxide. The liquor is then allowed to stand till the calcium carbonate and calcium soaps have settled, the clear solution

being syphoned off A considerable quantity of organic matter is carried down with the precipitate, but much remains still in solution In a German patent (311933, 1917) the liquor is heated under pressure at a temperature of from 250° to 300° C for two hours, which causes much of the dissolved organic matter to be precipitated as a carbonaceous deposit It is said that regenerated lyes contain sufficient reducing substances (possibly oxycelluloses) to protect cellulose from oxidation from the dissolved oxygen present in the fresh lyes Freiberger (*J Soc Dyers and Col* 1922, p 25) recommends the following process The liquor is boiled in the kier with lime and sufficient bleaching powder to turn the solution yellow without increasing its oxidising power A solution of a bisulphite is then added till the chlorine is reduced, indicated by the discharge of the yellow colour The precipitated organic matter and calcium compounds are then allowed to settle and the clear liquor is drawn off

The Efficiency of the Lye-boiling Process.– In the laboratory, working with say 100 grammes of cotton, the lye boil can be relied upon to do all that is required of it But in practice it is not a highly efficient process Moreover, it is the most costly operation in cotton bleaching From what has been said already, it will have been concluded that the lye boil removes proteins and pectins quite well But it cannot be relied upon to remove all of the cotton oils and waxes

One of the troubles of the cotton bleacher is that the bleached goods sometimes become yellow on storing One cause of this has been referred to, namely, the gradual decomposition of calcium and magnesium soaps whose presence is due to the use of hard or incompletely softened water But this "yellowing" occurs in the absence of calcium and magnesium soaps Other causes will be discussed in a later chapter, but one of them must be referred to here In very many cases this discoloration is undoubtedly due to residual impurities which should have been removed by the lye boil, but which, owing to the limitations of the process, cannot be removed always with certainty

There has been considerable discussion as to which of the unremoved constituents of cotton cause this yellowing It was believed, at first, that the nitrogenous constituents constitute the chief factor in its production Cross and Bevan associated it with the gradual decomposition of chloramines Hebden (*J S C I*, 1914, p 959) states that proteins are chiefly responsible for yellowing, but that ether-soluble impurities have also some effect, although those soluble in alcohol, after removal of ether soluble bodies, have not This means that while proteins are the chief cause, the cotton waxes have also a contributory effect Levine (*J S C I*, 1916, p 687) agreed with the conclusions of Hebden, but considered that traces of proteins are the chief cause He states that chloramines can be detected in cotton even after prolonged boiling with alkali But Higgins (*loc cit*) has shown that the proteins are practically always removed by the lye boil On the other hand, the fats and waxes are not Freiberger (Higgins, *Bleaching*, p 37) regards β oxycellulose as the main cause The balance of evidence now favours the view that traces of unremoved cotton wax are the all important cause of yellowing In nearly every case examined by the author, wax has been present and can be extracted by means of boiling benzol, with improvement of colour On the other hand, chloramines have been detected very rarely. When it is remembered that the colour of the cotton waxes isolated by Schunk, Knecht, and others varies in colour from yellow to dark green, that their melting-point is as high as 67° C, and that they are only completely saponified by heating with potassium hydroxide and glycerol, it is not surprising that they are difficult to remove completely by a dilute aqueous

solution of sodium hydroxide even at an elevated temperature The colour of all these waxes is darker when melted than when solid When fabrics are stored, traces of unremoved waxes work their way gradually to the surface of the goods and become visible Higgins (*J S C I*, 1914, p 902) states that these waxes are only gradually removed during the bleaching process, and that their appearance and colour are only altered slightly Hence, on heating the cloth at any stage of the bleaching process, it will become darker in colour owing to the melting of the waxes it contains Good scouring removes a large proportion of the non cellulose constituents, so that it is evident that the more perfect the scouring the less chance there is of yellowing on storing In fact, good scouring is the only method of preventing it But, as stated already, complete extraction of the waxes by means of the lye boil is an ideal which is very difficult to attain Hence modern research has been directed largely towards the replacing of the lye boil by a more certain process Added importance was given to this by the observation of Fort (*J Soc Dyers and Col*, 1921, p 162), that if as little as 0·1 per cent of fatty matter is left in piece goods it may be quite impossible to obtain a good beetle finish, yet if this residue of fatty matter is completely removed, the beetling can now be carried out satisfactorily Now, the only certain way of removing the last traces of oil and wax from cotton is to extract them by means of an organic solvent such as benzol or petrol This led to the patenting by Lumsden, Mackenzie, and Fort of the use of an organic solvent boiling above 100° C for the degreasing of cotton goods for bleaching and finishing Solvents with a higher boiling point than water (Brit Pat 170544, 1921) are said to be superior in cleansing powers to those boiling at lower temperatures, and have the further advantage that the goods need not be dried, the moisture being driven out during extraction

Higgins (Eng Pat 131798, 1918) also patented the use of volatile organic solvents for the scouring of cotton, while Peckham (*J S C I*, 1916, p 203) proposed to boil the goods in a solution of benzol or petroleum in an aqueous solution of soap, *e g* 50 gallons of water containing 10 lbs of soap and 3 gallons of benzol It must be noted, of course, that extraction of grease, by means of a solvent, does not do away with the necessity for some form of alkaline treatment But it does make the cumbersome high pressure boil unnecessary When once the oil and wax are removed the nitrogenous constituents can be dissolved quite easily by means of a mild alkali such as sodium carbonate boiling at ordinary pressure, and the same applies to the pectins and other soluble impurities Thus no caustic soda is required The following extract is taken from Fort's paper —

"The extended use by manufacturers of non-saponifiable sizing ingredients, such as soft paraffin and other tallow substitutes, which do not yield to reasonably good scouring, has been troublesome enough to the bleacher but a veritable curse to the beetle finisher who is required to attain a high standard in the beetling of these goods Caustic boiling, in most cases, can be made to give a satisfactory bottom for white either on linen or cotton, but if paraffin wax is present, will not likewise ensure the best finish, and repeated lime boiling of such goods has also failed to yield the uniformly good beetling qualities desired Solvent extraction, in conjunction with bleaching, relieves the bleacher of an intolerable burden, namely, the necessity of using unduly severe treatments, which have not always been required to gain the necessary white, but seemed to be called for in the interests of the finish Preliminary solvent treatment also facilitates every one of those treatments (*i e* alkaline treatment, bleaching, etc) to a greater or less extent, rendering them more effective, as the waxy impurities, if not removed, retard penetration by wet agents, and, moreover, can combine

with chlorine or its compounds, and thus interfere with the success of chemicking and scouring. The complete absence of wax and grease in either full or half-bleached goods, which have been extracted, assists in obtaining a maximum degree of permanence and freedom from defects arising in storing."

In a later patent by Lumsden, Mackenzie, and Fort (*J Soc. Dyers and Col.*, 1925, p 33), it is claimed that bleached yarns and fabrics of vegetable fibres having special features are obtained by treatment with hot organic solvents, followed by bleaching, without the usual boiling with lime or caustic alkalis. Instead of ordinary bowking operations, a scouring with lime or caustic alkalis is carried out, in the cold, or at temperatures lower than the boiling-point, with or without the addition of bleaching or other known agents suitable for use in scouring baths Subsequently, known bleaching treatments are given, and bleached goods are thus obtained remarkably free from oil, fat, wax, and various other impurities, but nevertheless consisting not only of cellulose conserved to the greatest possible extent, but also containing certain natural non-cellulose impurities which are retained in the interest of weight by this process.

There was some prejudice, at one time, against solvent extraction on account of waste of the solvent and danger of fire These have now been overcome The risk of fire is very small, and non-inflammable solvents are also available, while modern degreasing plants do not waste more than 0·5 per cent of the solvent used.

The apparatus used in degreasing will be described in Chapter XX.

The treatment of degreased goods with a proteolytic enzyme for the removal of proteins has been suggested and claimed by several patents. Levine (*J S C I*, 1916, p 687) found that several different species of bacteria, such as *B amylolyticus*, *B. fimi*, *B bibulus*, *B carotovorus*, and *B. subtilis*, secrete enzymes which are able to render the proteins of cotton soluble and also the ether-soluble impurities He suggested treating cotton goods with a culture of one of these organisms for from twenty-four to seventy-two hours The destructive action of many bacteria on cotton referred to in Chapter X would make the use of this process very dangerous But this objection would not apply to preparations of the enzymes themselves. Pancreatin is the simplest and most readily obtainable of these. Its use is claimed by several patents, though it seems doubtful whether some of them can be valid Thus, Rohm (Eng Pat 100224, 1916) patented the steeping of cotton for some hours in a 0·1 per cent solution of pancreatin at a temperature of 20° to 40° C He claimed also the use for the same purpose of other agents such as the fresh pancreas of animals, papayotin or papan fruit, the enzymes of the castor-oil seed, etc

The patentees of the use of enzymes generally claim more than can be accomplished Thus, Rohm states that boiling with alkalis can be omitted altogether, mere washing with water after the enzyme treatment being recommended Proteolytic enzymes render proteins soluble by changing them into simple amino compounds, but it is very doubtful if they decompose the pectins, and certain that they would not remove the cotton waxes. The pancreas secretes a fat-splitting enzyme which in the presence of sodium carbonate converts readily saponifiable oils into soaps, but even in the human body a considerable proportion of the saponifiable fat taken as food passes out quite unchanged.

CHAPTER XVIII.

KIERS.

Simple Kiers.- The kier is the most important of all the apparatus used by a bleacher. It is the name given to the special vessel in which the saponification of the fats and hydrolysis of the proteids and other natural impurities of the cotton are carried out by boiling in the presence of alkali The simplest form of kier is a household copper in which the goods are placed and heated, by means of a fire underneath, with soap and carbonate of soda, circulation of the liquor being ensured by occasional stirring with a wooden staff or dolly To prevent the loss of heat the copper is covered with a lid, water being added from time to time to replace that lost by evaporation. Kiers constructed on these simple lines were originally used in bleaching, but they had so many obvious disadvantages that their use was soon given up Direct heating is both inconvenient and wasteful for large quantities of goods where circulation is rendered difficult by reason of the mass treated The direct contact of cotton goods with the heating surface again causes local overheating and burning Thus indirect heating by means of steam, accompanied by an automatic method of producing circulation of the liquor, was gradually introduced, and subsequently followed by boiling under increased pressure in a closed vessel to diminish the time necessary for saponification and to economise heat These improvements have been followed by others having for their object the easier manipulation and equality of treatment of the goods during the boiling process Sometimes the liquor is heated entirely outside the kier and circulates from the external heater through the kier and back again to the heater Kiers are sometimes constructed of wood, but generally of cast iron or steel They may be adapted for either low or high pressures They are often heated by direct steam, but preferably by a set of steam pipes, which are either placed in the kier itself or outside The outside of the kier is sometimes coated with wood or some non-conducting material to prevent loss of heat by radiation

The most important mechanism in the kier is that which maintains the temperature and circulation As we have seen in a previous chapter, if large quantities of goods are boiled in an alkaline solution, the liquor follows the line of least resistance, and the denser portions of the goods do not become penetrated The devices for securing adequate circulation are very numerous Many of them will be noticed in the following pages in connection with special kiers, but it is hardly possible to include all the forms of kiers that have been proposed.

Improved Kiers.—In comparing the efficiencies of kiers of different types it is instructive to note the conditions under which the heat or kinetic energy of the steam may be expended. This expenditure occurs in (1) heating the contents and metal work of the kier up to the working temperature and making good the losses occurring through radiation or evaporation, and (2) in maintaining a relative movement between the liquor and cloth, more usually a circulation

of the liquor The greatest and most rapid expenditure of heat commences as soon as the steam is applied to the kier, and continues until the contents have attained the desired working temperature and the pressure corresponding therewith An approximate measure of this initial heat demand, which is useful for estimating the necessary steam, is given by the following formula —

$$H=(T-t)\left(W+\frac{w}{10}\right),$$

where

H=heat units (kg × ° C),
T=working temperature ° C of the liquor,
t=initial temperature ° C „ „
W=weight of the liquor,
w= „ „ kier

Having obtained a numerical value of H, corresponding to assigned values of the terms in the above formula, the requisite expenditure of steam to yield H heat units may be calculated by means of the following table —

Temp , °C	Pressure, lbs per sq in	Sensible Heat, kg °C per kg Steam	Latent Heat, kg °C per kg. of Steam	Total Heat kg. °C per kg Steam
100	14 7	100 5	539 1	639 7
105	17 5	105 6	536 1	641·7
110	20 8	110 7	532 9	643 6
115	24 6	115 8	529 8	645 5
120	28 8	120 9	526 6	647 4
125	33 7	126 0	523 3	649 2
130	39 3	131 1	520 0	651 0
170	115 3	172 2	491 4	663 7

This table gives the properties of steam at various temperatures and the extent to which heat is stored in the steam The sensible heat is that which is required per 1 kg of water to bring it from 0° C to boiling-point at any given temperature, and the latent heat is the further heat which must be imparted to it to convert it to steam at the same temperature The total heat is the sum of these two quantities

When steam is passed directly into liquor at a lower temperature than itself it immediately condenses, and transfers to the liquor the whole of its latent heat

The condense mingles with and dilutes the liquor, and in dropping to an equal temperature yields to the liquor a quantity of heat equal to the weight of the condense, multiplied by its drop in °C of temperature

The weight W_s of live steam in kg at any given temperature of supply T_s in °C which must be injected into the liquor to raise it from t to T is found by dividing the known value of H by the total heat of 1 kg of steam at temperature T_s, less its sensible heat at temperature T The quantity of liquor is thereby increased by the amount W_s, and the heat expenditure is $H+W_s \times T$ heat units

When the heat of the steam is only transmitted to the liquor through an intervening heating surface in a calorifier it is practically only the latent heat of the steam which is transferred to the liquor The sensible heat remains in the condense, which, being kept apart from the liquor, may leave the calorifier at

or near the steam temperature The quantity H is in this case divided by the latent heat only, and the weight of steam required is therefore greater. This does not imply a greater nett heat expenditure if the condense be returned directly to the boiler, but if this is not done the loss may be appreciable because of the increase of sensible heat with increase of steam pressure, and the desirability of using high pressure for such indirect heating appliances.

A further expenditure of heat arises during the heating up of the liquor to balance the loss due to radiation from the external surface of the kier. This loss continues throughout the boiling process It can, however, be limited, by the application of suitable insulating covering to the exposed metal work of the kier and its pipework, etc , to 2 9 of a kg. ° C heat unit per hour per square metre of radiating surface per ° C difference between the temperature of the liquor and the external air

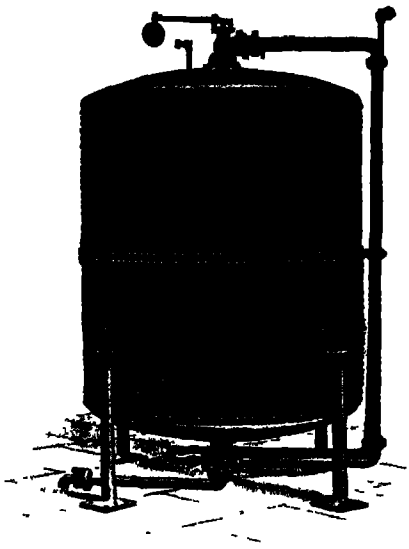


Fig 105 —High-pressure kier with external injector circulation (*Lang, Bridge, Ltd*)

The efficiency of an injector lies in the conversion of the kinetic energy of the steam passing through it into heat energy, which passes into the liquor after the performance of mechanical work But when the working temperature of the liquor is reached and cannot be exceeded for the reason given later, no further absorption of heat from injector steam is possible, and it passes uncondensed through the liquor As continuous circulation is essential, it is usual to restart it when thus arrested by wastefully lowering the temperature of the liquor

In open kiers an additional and more appreciable loss takes place partly by evaporation of liquor from the open top of the kier, and also by the escape of live steam through the puffer pipe, unless the regulation of steam thereto is carefully checked. These losses can be determined only by deducting such steam expenditure as can be estimated from the total supply of steam to the kier The simplest measurement of the total supply is by metering the water evaporated in a boiler supplying only the kier under test, during a complete process

The operation of circulating the liquor is in more modern kiers performed mechanically by a centrifugal pump, and the power expended can be measured most conveniently if the pump be electrically driven In the simpler kiers both heating and circulation are effected by steam acting through a puffer pipe or an ejector, as described later This method has the disadvantage of making these processes inter-dependent, whereas they should be under separate control Although most admirably adapted both in simplicity and efficiency for the combined performance of circulation and heating during the process of heating up the liquor, an injector becomes afterwards uncertain in action and wasteful of steam.

Injector Kier.—From a mechanical point of view the injector kier is the simplest, being readily adjustable to both low and high pressures.

It consists of a cylindrical steel shell (fig 105) with dished ends, the lower of which is covered with an iron grid or false bottom In the upper are manholes for the entry of the goods These are provided with covers placed on the inside

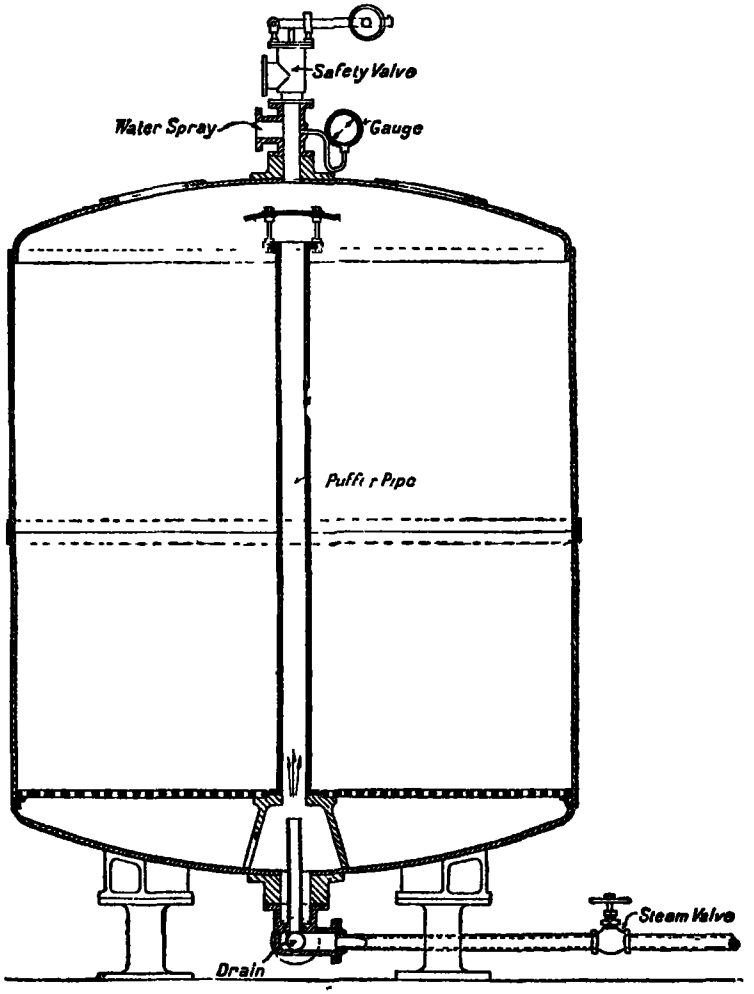


FIG. 106.—High-pressure kier.

and fastened by a bolt which passes through a saddle spanning the manhole externally. The circulation is produced by means of an apparatus somewhat similar to the steam injector of a boiler. This may be either outside the kier, or the circulating pipe and injector may be placed inside at the centre, in the form known as the puffer pipe, as shown in the kier of Messrs J Walker & Sons, Ltd. (fig. 106).

A simple form of injector is shown in fig. 107. It consists of a water chamber A,

with an orifice the shape of which resembles that of two inverted cones Within the chamber, and placed concentrically with the conical orifice, is a conical steam nozzle The chamber and nozzle are fed by a liquor and a steam pipe respectively On issuing from the cone, the steam enters the surrounding cone, where it meets the liquor The contact of the liquor and steam produces two results (1) the steam, which emerges with great velocity due to its pressure, communicates part of its velocity to the liquor; (2) at the same time the steam is condensed by the lower temperature of the liquor, so that, at the extremity of the cone, practically the whole of the steam is condensed and a column of liquor emerges. The peculiar shaping of the orifice is favourable to the utilisation of the velocity of the steam and prevents the occurrence of eddies which would dissipate the energy of the steam

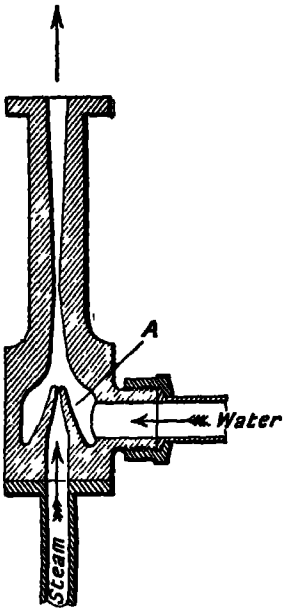


Fig 107 —Injector

For low pressures the kier is made in the form of an open iron pan, with or without a light movable lid, provided with an exit pipe to remove steam, prevent undue loss of heat and access of air to the goods in the kier The circulation and heating produced by an injector or steam elevator differs from that given by the "puffer"

The injector within limits of its adjustment, depending on the temperature of the liquor and the pressure against which it is acting, gives continuous circulation for a smaller expenditure of steam, since the cones of the injector are proportioned to utilise the velocity of the steam in an efficient manner The heating of the liquor is only effected gradually and requires longer than with the puffer.

The puffer consists of a conical base fixed in the well and to the bottom of the kier, with apertures for inlet of liquor that has drained through the cloth into the well On this base is fixed a substantial vertical pipe of 4- or 5-inch bore, surmounted by a spreader or bonnet A steam nozzle rises in the centre of the base just entering the discharge pipe, the height of the steam nozzle requiring careful adjustment to secure the best results The effect to be specially avoided is the discharge of steam into the well instead of up the discharge pipe In operation, the well-liquor rises in the pipe and finds a certain level depending on the quantity of liquor in the kier The steam from the nozzle discharging into this column heats and expands it until a stage is reached when the steam, ceasing to be condensed, ejects the column of liquor bodily from the discharge pipe and up against the bonnet spreader, by which it is deflected with a thud on to the top of the cloth. Meanwhile a fresh column of cool liquor rises in the tube and allows a subsidence of the cloth which was previously, and in a relative sense, floating This effect is more apparent with heavy than with spongy cloth As the hot liquor penetrates the cloth, the original state of affairs is regained, and these operations are continually repeated with this series of motions of the cloth. When this so-called vomiting action is confined within reasonable limits, it is found to have a beneficial action on the effective application of the liquor to the cloth, and doubtless results in repeated changes in the mode of contact of

liquor and cloth, opening out new courses and squeezing or draining out those parts that had become saturated It is at any rate evident from this action on goods containing certain coloured headings that the effect of this motion of the bulk is to discharge these colours in a way which does not occur with gentler circulation

The boiling of cloth in kiers circulated and heated by live steam demands rather careful attention and manipulation of the steam inlet valve The lifting capacity of an injector decreases with the rise of temperature of the liquor and of the pressure against which the liquor has to be forced, and while the discharge from the puffer pipe is less impeded by rise of temperature, there is liability in both cases to a discharge of steam only, with overheating of the cloth, especially if it comes into contact with the puffer pipe This discharge occurs whenever the temperatures of the liquor and steam are the same To prevent damage from this cause the puffer pipe is generally lagged externally with a protective covering of wood or sacking Similarly, the iron grids are sometimes covered with well rounded stones to keep the cloth away from the iron grid When the steam pressure at the top of the kier is in excess of that in the well, steam must be checked or stopped till equilibrium occurs, and the boiling circulation then carried on at a more moderate rate When the circulation in an open kier is checked for lack of liquor in the well, due to shortness of liquor or prior to its expansion and augmentation by condensed steam, and because the flow through the cloth has not attained the normal rate, the attendant or ' Bowker has recourse to replenishing the well by means of a bypass of liquor This is effected by the insertion of a perforated vertical trough or a stout wooden beam during packing between the cloth and side of the kier, which beam he agitates to make a groove for the liquor to flow down Though an apparently foolish procedure, as ignoring the purpose of circulating, it serves to prevent overflow and loss of liquor, and also to divert it from places where it might have become stationary or air locked It also prevents access of steam to the bottom of the cloth through the well becoming empty and affording an open course from the steam inlet

In all closed or high pressure kiers precautions must be taken to avoid the blocking of the outlet to the safety valve by stray laps of cloth This is sometimes caused by the contents being subjected to a greater pressure from beneath than from above, thus causing a general rise of the contents This, however, cannot happen where there is a positive downward circulation To secure this, the packing must be carefully done, and the top of the cloth may be covered with a jute sheet well loaded with stones or fastened by chains, but still allowing reasonable room for expansion In addition, the openings to the safety and air valves should be protected with a perforated bonnet, or the air valve may be placed in a different position so as to allow alternative outlets Care must be taken that the readings of the pressure gauge are not falsified by such obstructions as above mentioned, and the kier subjected to excessive pressure and danger of bursting or overheating of the cloth If at the end of the boil the steam be liberated too quickly at first, the sudden reduction of pressure at the top of the kier may cause clogging of the valve Cases have been actually known in which the top of the kier has been blown off through this cause, contributed to, perhaps, by the use of a hinged lid instead of one of the self-closing type.

In order to ascertain the state of the liquor during the process, test-cocks are fixed at suitable points If on opening a test-cock steam escapes, it indicates that the goods are being exposed to danger of overheating, and the circulation must at once be increased

Numerous improvements have been proposed with a view to overcoming

the difficulties of pressure and circulation, such as relieving the pressure at the top of the kier by an automatic equilibrium valve, or by connecting the top and

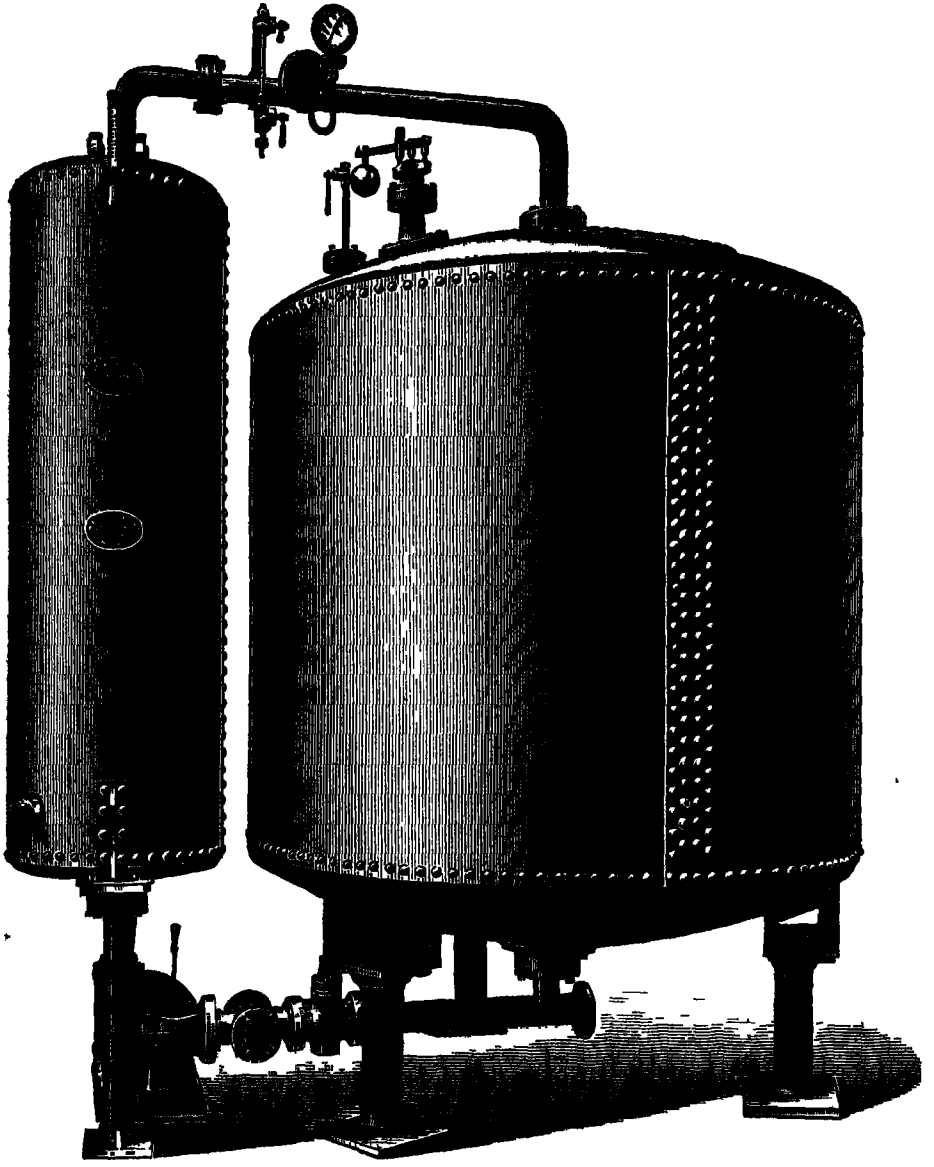


FIG 108.—Walsh's bleaching kier

the well by means of a centrifugal pump or bypass. In some kiers the circulation is given to the cloth itself, the liquor remaining stationary. Other improvements have for their object the shortening of the time necessary for boiling and

handling of the goods. In the low-pressure kier the time of boiling is in some cases twelve hours, without reckoning that necessary for cooling and removing the goods. In more modern and special forms of high-pressure kiers this may in certain cases be reduced to about two hours.

The following are examples of some of these special forms of apparatus .—

The Walsh Kier (fig. 108) consists of the usual steel shell, an external tubular heater and centrifugal pump. A circulating and drain pipe is fixed to the well, and at the top end of the kier are inserted the usual bonnet or spreader, surmounted by a block and branch, fitting on which are safety- and air-valves, pressure gauge, as also liquor circulating and water pipes.

The heater contains tubes which separate the liquor and steam, the latter warming the liquor by conduction of its heat through the tubes.

This type of kier is a very satisfactory one in regularity of circulation, general reliability, ease of control, and the thorough boiling of piece goods which are suitable for treatment in rope form.

This is due to the positive mechanical circulation of the liquor, to the separate control of the heating, to the separation of the live steam and attendant impurities from the cloth, and finally to the freedom from dilution of the liquor by condensed steam, thus avoiding the necessity of compensating for this by reducing the initial charge of liquor.

Greater confidence is thus afforded in the treatment of goods which are out of sight in a closed vessel, and in the adoption of high boiling temperature for the more thorough bottoming of the goods, and the shortening of the process.

However, to credit any shortening of the process directly to the heater is inaccurate ; for unless the transmitting surface within the heater is considerable, the process of heating up the liquor is retarded owing to the low rate of heat transmission from the steam to the liquor through the metal walls of the tubes

To obtain a reasonable rate of transmission, it is necessary to maintain rapid circulation of liquor and the maximum possible difference of temperature between the steam and the liquor.

Elevation of steam temperature is restricted only by the strength of the heater to withstand the corresponding steam pressure

The relationship between pressure and temperature of steam enables the desired working temperature of the liquor to be definitely fixed by the setting of the safety-valve. Immediately that temperature is exceeded the safety-valve opens, thus preventing any further rise of pressure, and consequently also of temperature When this happens the supply of steam to the heater is adjusted to equalise the small but continuous heat losses from the kier by radiation, and thus maintain the required working temperature.

The chief defect as regards pump-driven circulation lies in the low mechanical efficiency and the wear and tear of the pump Against this, however, may be set the actual economies resulting from the subdivision of steam expenditure for heating and driving and the positive circulation guaranteed. In view of the somewhat great energy of circulation, the contents of the kier are generally supported by cross struts, which tend to prevent entanglement of the cloth. This, if it happens, causes great difficulty in the subsequent extraction of the goods.

Mather and Platt's Kier has an external contact heater, and circulation is maintained by a centrifugal pump, which continuously withdraws the liquor from the kier and sprays it again on to the goods A number of pipes and valves permit of the boiling or washing liquor passing through the goods in every direction.

It is illustrated in fig. 109. It is made in sizes varying in capacity from 1½ to 3½ tons, and is constructed for a pressure of 40 lbs per square inch, being tested up to 80 lbs It is made in the form of a horizontal iron cylinder with doors, N, which are raised or lowered by the gearing shown above The goods are placed in two wagons, A and A They are saturated with soda solution before being packed in the wagons, which are then run into the kier through the door raised for the purpose Each kier is provided with two sets of wagons in order that whilst one set, filled with the goods, is being treated, the other may be emptied

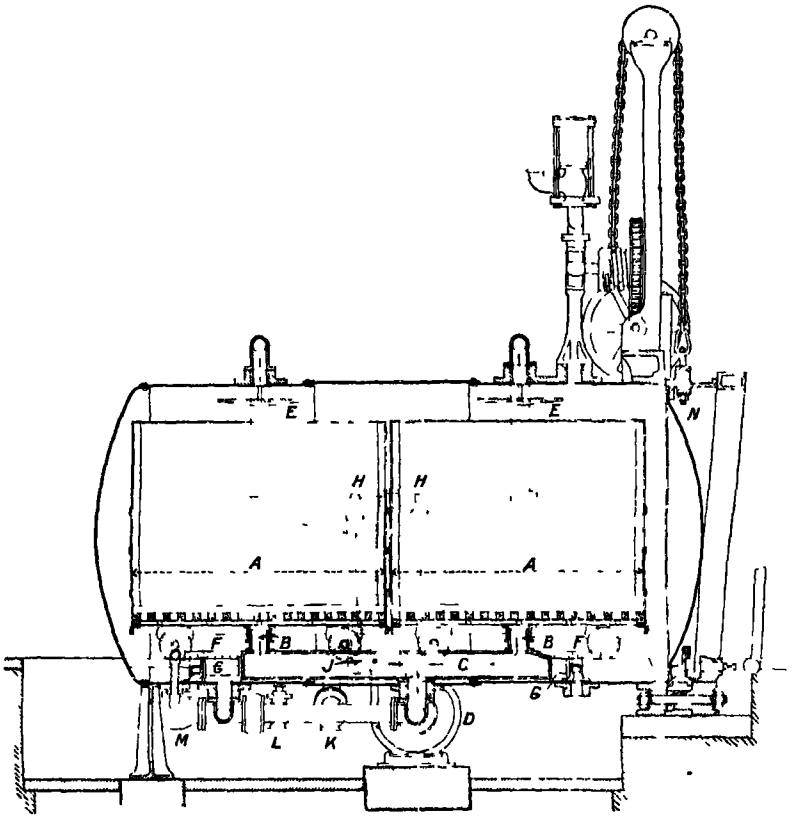


FIG 109.—Mather and Platt's kier

and refilled for changing as soon as the boiling is finished The changing of 3 tons of cloth occupies less than ten minutes instead of an hour or more, as is the case with ordinary kiers, and the working is therefore continuous The circulation is effected by means of a powerful centrifugal pump D, and, by means of the valve H and J, the direction of circulation can be altered at will. The horizontal arrangement of the goods and the small depth to be penetrated ensures thorough circulation of the boiling liquor. The liquor falls on to the goods in the wagon through the spreader E. It percolates through them and leaves through the outlet B, which returns it to the pump through the pipe C.

The heating of the liquor is effected by means of direct steam injected through

perforated pipes, F, and by indirect steam passing through a coil pipe (G) placed

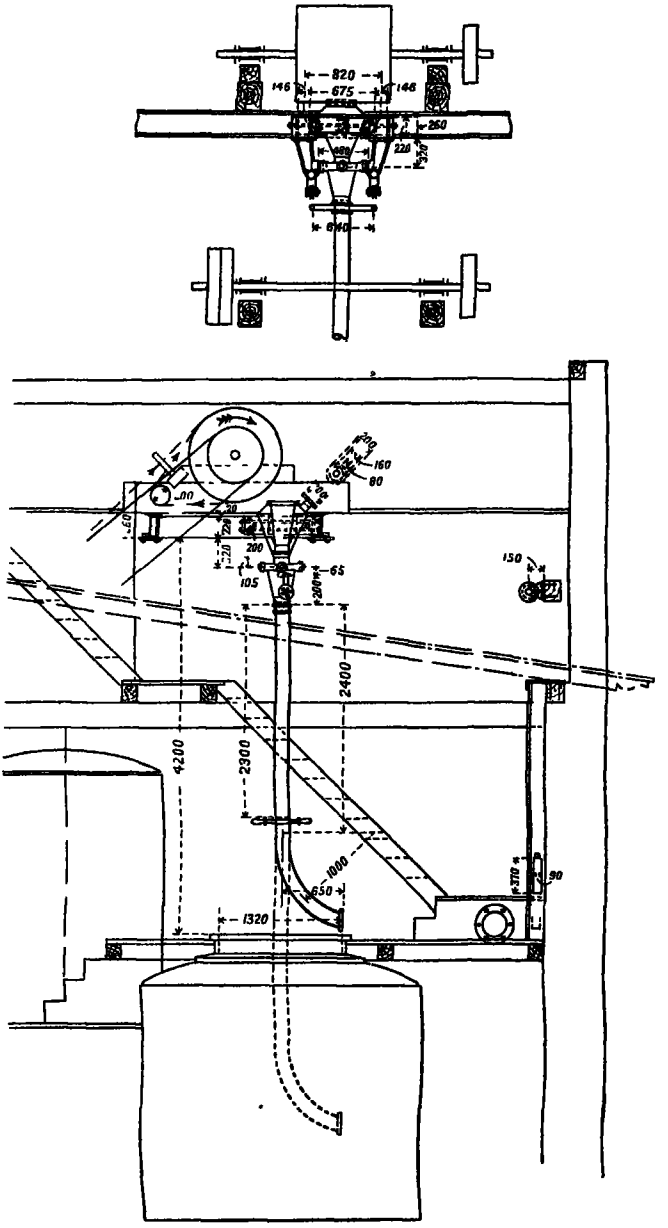


FIG 110.—Thies-Herzig kier and plaiting apparatus.

in the bottom of the kier. A modification is also made in which an outside multitubular heater replaces the internal heating pipes, and a vacuum pump

may be added, if necessary, to withdraw air previous to commencing the boiling. When the boil is complete, the liquor is drawn off through the outlet M, and the goods are washed in the kier by means of water introduced through the inlet valve K. The washing of the goods before they are removed from the kier is a very important point, since it prevents all danger of damage caused by concentrating soda solution or the action of air and alkali on the cotton

Thies-Herzig System of Sir James Farmer & Sons, Ltd (fig 110).—In this system the boiling process is characterised by the employment of a strong caustic lye, together with a special mechanical method of plaiting and impregnating the cloth in the kier, which has already been described This process of plaiting and impregnation not only conduces to regular and effective circulation, but also prevents the imprisonment of air in the folds of the cloth or its access during boiling.

The cloth undergoes a preliminary process of scouring in a warm sour, the elevation of temperature intensifying and accelerating its action This preliminary scour is carried out very expeditiously by employing three machines in tandem. In the first and third of these the cloth is washed with water, and in the intermediate one it is treated with dilute hydrochloric or sulphuric acid at a slightly elevated temperature The strength of the sour employed is 16 grammes of 30 per cent hydrochloric acid, or 10 grammes of 60 per cent sulphuric acid per litre A little hydrofluoric acid may also be added to dissolve silica This acid treatment removes most of the mineral impurities, and causes the lye in the subsequent boiling to remain clearer than is the case in most other systems. The cloth is now transferred to the kier by means of the special mechanism, and at the same time impregnated with the lye Any high-pressure kier, which affords effective circulation, may be used, but it is necessary to provide a wide circular central opening in the top end of it for the introduction of the telescopic feed tube of the impregnating and plaiting apparatus This tube is directed by hand, and can be raised, lowered, or swung into any required position by means of a universal joint by which it is suspended

It is said that the plaiting is so regular that kiers of fifteen tons' capacity may be used without difficulty When the kier is full the telescopic tube is withdrawn and the kier sealed Circulation of the strong lye is maintained by any suitable method. Upon completion of the boiling process the liquor is withdrawn, the kier being meanwhile washed out with hot water The remaining processes of chemicking and souring are then carried out, together with the necessary washings, in sequence No piling is necessary, owing to the completeness of the boil This is said to be so thorough that only very weak chemics (about one-third of the ordinary strength) are necessary, thus avoiding danger of overbleaching, while even with goods most difficult to bottom, repetition of the processes is rarely necessary

In the earlier processes the goods were treated with a solution of magnesium or calcium chloride before introducing them into the kier This causes the liberation of calcium or magnesium hydrate in the fibres, which is said to protect them from mercerisation by the concentrated soda lyes employed (5 to 7 per cent). In later processes it is claimed that the complete absence of air, which is ensured by the special method of impregnation and plaiting, prevents any danger of mercerisation, and of course the production of oxycellulose. The importance of the absence of air in lye boiling has already been referred to, and also the necessity or desirability of removing the lye, at the end of the boil, without undue exposure.

The use of warm sours is, in itself, now new, and has not always been regarded

with favour. Warm sours, however, must have the advantage of increased chemical activity, thus allowing them to act to a fuller extent in the limited time in which the cloth is exposed to their action, besides, owing to their weakness, leaving less acid to be subsequently removed.

In dealing with the changes occurring during the soda boil, it was stated that the strength of properly boiled cloth was always greater than before boiling, and that incomplete boiling, which necessitates severe bleaching, is frequently productive of overbleaching or loss of strength.

This contention seems to be confirmed by the Thies-Herzig process, in which it is said that the cloth is always about 20 per cent stronger after bleaching.

Jefferson-Walker Kier.—This apparatus consists of a high-pressure kier and an automatic live steam positive circulating arrangement outside the kier.

The method of operation consists in the periodic withdrawal, heating, and return to the kier of successive charges of liquor The incidental variations of steam pressure and level of liquor in the kier give rise to conditions subsequently referred to, which are claimed to increase the rapidity and effectiveness of the boiling process.

Referring to figs 111, 112, and assuming the kier (1) to be packed with cloth and charged with liquor, the effluent drains through pipe 2, check valve 3, and pipe 4 into a receiver 8.

It rises simultaneously in 8 and pipe 25, then onwards through pipe connections 26, 28, 29, until it charges the hollow ball 30.

This ball, together with parts 26, 28, 29, and 31 to 35, forms a balanced framework free to oscillate through a small angle about the pivot 38, and counterpoised by the counterweight 39.

The result is that when the ball 30 is charged, as described, with liquor and overbalances the counterweight 39, the steam valve 43 is opened Steam now passes from valve 48 through pipe 46, valve 43, pipes 47 and 56, enters the receiver and drives out the charge of liquor through the pipes 4 and 5, and a check valve at 6 (controlling pipe 5) to the spreader 7 at the top of the kier Meanwhile the ball empties by pipe 25, and the liquor is replaced by steam flowing through 35, 36, 33, 31, and the counterweight 39 causes the oscillating system to close the equilibrium valve 43 by means of link 42, and steam is shut off Any excess of steam escapes by 44 and 45 and check valve 45′ into the kier, also via 56 and check valve 55. The receiver is now isolated by check valves 6 and 45′ from the top of the kier as regards any return of steam through pipes 5 and 45 respectively As the residue of steam in the receiver condenses, a partial vacuum or less pressure than that in the kier obtains in the former, and either assists by suction, or permits of the flow, of a fresh quantity of liquor from the base of the kier. Entering the top of the chamber 6 is a steam nozzle, which supplies heat to the circulating liquor, in addition to that gained from steam in the receiver; it also expedites the flow of liquor. At the commencement, when the liquor is cold, this injector is sufficient to start the circulation, and when it fails to do so the receiver apparatus automatically takes up the operation When the steam remaining in the ball and receiver offer any back pressure to the rise of liquor, such steam is released into the top of the kier through pipes 41, 44, and 56, and chamber 55; these feed into the common pipe 45, whence the steam passes upwards through check valve 45′, and so into the kier.

The object of chamber 55, which contains a ball valve controlling access to pipe 45, is to close it to the passage of high-pressure steam from valve 43 during

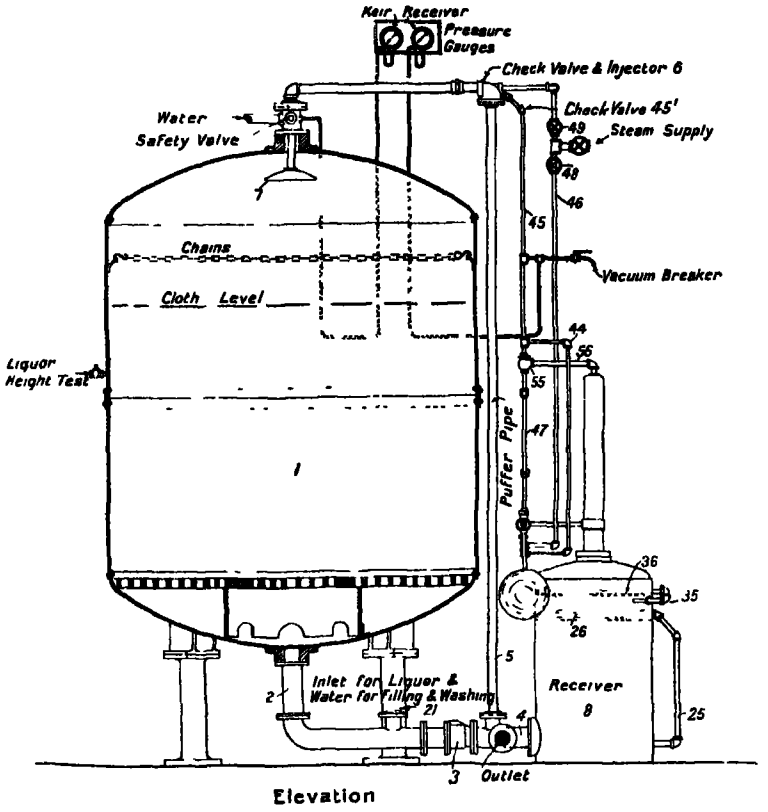


FIG. 111 —Jefferson-Walker kier.

the discharge of liquor from the receiver, but when valve 43 closes, the drop of pressure releases the ball valve and permits of the action previously described

The pipe 45 contains a branch and stop valve for liberating air when the receiver is first filled, and for admitting air when the process is over and the receiver is to be emptied.

It is essential that the pressure of steam supplied at valve 48 shall exceed that in the kier, and suffice to overcome the head and friction encountered in ejecting liquor from the receiver. This condition, together with the multiplicity of valves, is the chief drawback to the apparatus, which otherwise affords a compact and automatic means of producing a very efficient and positive circulation without recourse to mechanical pumping

Apart from the ingenuity of the circulating system, the point of chief interest is the manner in which the intermittent discharges of liquor cause the cloth to rise and fall as the kier is successively flooded, and a portion of the liquor discharged into the receiver

This action is analogous to that occurring in the vomiting kier, and is found, to the author's knowledge, to give excellent results where reasonable attention is given to the operation of the apparatus

The action which occurs during circulation, etc, may be considered in further detail as follows The cloth is plaited into the kier, secured by the chains at the top to prevent undue movement, the manholes closed, and the liquor entered from an external mixing and warming tank by way of branch 21 In the case of lime boiling, the liming is effected by a machine, and the balance of liquor added as stated. It rises through the cloth, expelling air-bubbles, and when it reaches the test-cock, a supply valve is closed, as also the cock The liquor meanwhile rises in the receiver, emptying it of air by air-valve in pipe 45, which is then closed. The air-valve at the top of kier remains open for a short time in the usual manner for the expulsion of air, for which purpose the valve 49

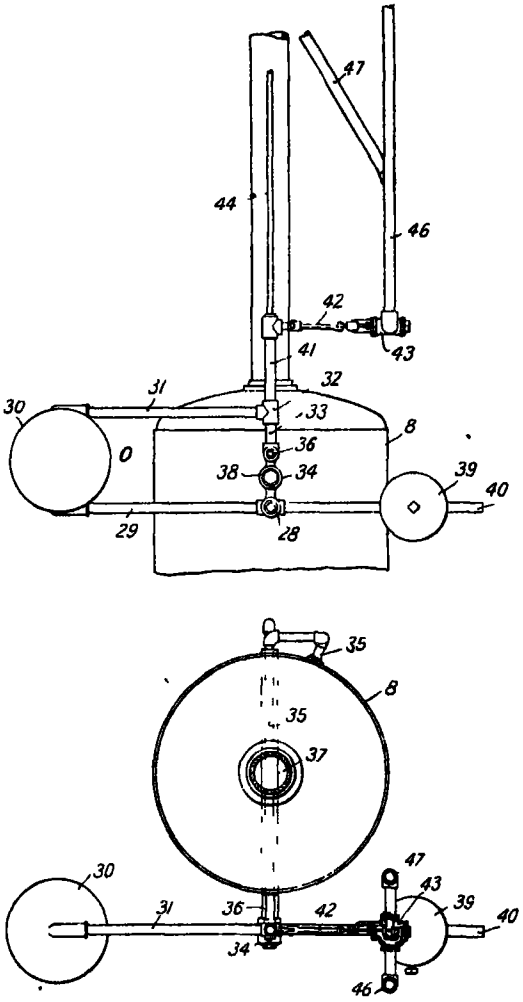


FIG. 112.—Jefferson-Walker kier. Detail of ball valve

may now be opened to fill the top space with steam. It will (if the liquor be cool) create sufficient suction to commence circulation of the column standing in pipe 5, and maintain a flow of liquor through it from the well of the kier by check valve 3; or the valve 48 may also be opened and commence the operation of emptying the receiver. This discharge meeting that occurring at the nozzle in chamber 6, is further heated The air-valve is presently closed, and the kier begins to get up pressure, being assisted thereto by the intermittent discharges from the receiver, and the continuous flow of steam from valve 49. This latter has the effect of applying a pressure at the top of the liquor covering or passing through the cloth Thus, for a period, the cloth exists in a state of compression, which is, however, momentarily relieved by a partial condensation of steam, when a discharge of cooler liquor from the receiver enters the kier, or an accumulation of liquor causes the cloth to "float" within the limits of the fastening chains. Now the reverse action occurs, as the liquor for the next discharge is drained from the kier, and the cloth sinks. The pressure above it rises again, and the state of compression supervenes When the pressure of the kier has reached the working limit to which the safety-valve is set, or before this stage, the valve 49 may be closed, the subsequent discharges being effected solely by the supply from valve 48, which feeds valve 43 When the temperature of the liquor fails to produce any appreciable condensation of the residual steam in the receiver, such steam is vented to the top of the kier in the manner already described, so that in any case it does not seriously retard the filling of the receiver during the gravitation of the liquor into it from the kier, nor offer any obstruction to the opening of the check valve 3 to permit this flow The function of this back pressure check valve 3 in directing the discharge from the receiver to the top of the kier is obvious The rate of circulation is indicated by the automatic oscillations of the ball lever, and by comparison of the pressures existing in the top of the kier and the receiver respectively, by means of gauges connected therewith It is claimed that a considerable saving of steam is effected through the reduction of time necessary for boiling owing to the rapid heating of the liquor and the peculiar motions occurring in the cloth by reason of the intermittent discharges of liquor, and the varying conditions of pressure between the folds of the cloth There would appear to be some foundation for the claim in respect of this effect being akin to that of the vomiting kier, and the rate of heating up is certainly superior to that of the tubular heated kiers The claim for extensive economy of steam by reason of its direct application to the liquor must be somewhat difficult to substantiate, as there does not exist any great margin of economy to be effected in this respect over the external pumping arrangement, considering the relative expenditures of steam which are required for heating and circulating.

The vomiting or periodic mode of circulation, together with its effects as noted in connection with the puffer pipe and with the Jefferson-Walker kier, may be further applied as shown in the two following schemes devised by the authors, to embody the combinations of effects to be respectively described

Vomiting Kier with Pump Circulation.—The combination of features in this case is as follows:—

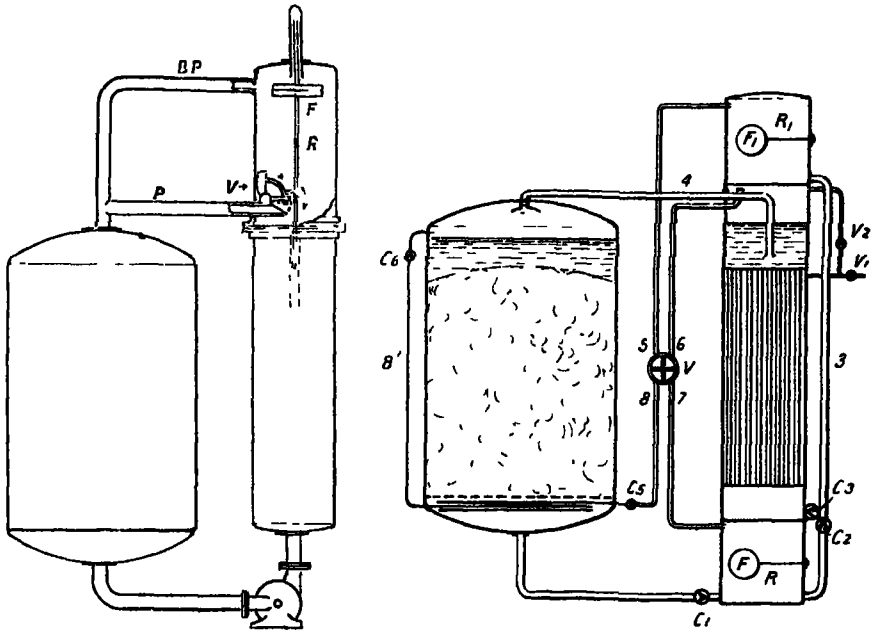
1 Elevation of the liquor by mechanical pump through an external tubular heater, and its subsequent periodic discharge

2 Corresponding effects on the cloth, such as are peculiar to the adoption of vomiting action, and to indirect heating of the lye as previously described

The arrangement is shown diagrammatically in fig. 113, and is in effect a kier of the Walsh type, with an extended dome to the heater into which the liquor is

continuously pumped. A suitable charge of liquor having accumulated in this chamber R, the float-controlled feed valve V is opened, and admits to the vomiting pipe P, through which the liquor rushes out by gravity to the spreader and thus on to the cloth, causing it alternately to float and sink. Upon completion of discharge, *i.e* when the float has dropped to a given level, the valve closes and the cycle of operations repeats itself

The bypass BP serves the double purpose of equalising the pressures in the chamber R and at the top of the kier, so that the rapidity of discharge is unaffected by such differences of pressure arising, and it further acts as a bypass in the event of breakdown of the automatic valve, in which case, or as required for certain goods, the operation reverts to that of continuous circulation.



FIGS 113 and 113A —Automatic circulating kiers

The valve may be set to effect any desired rate or period of discharge from that of the ordinary puffer pipe to that which corresponds to the full stroke of the float, or the capacity of the receiver. The objection urged against float-operated or other automatic valves is entirely met by the provision afforded by the bypass, and, given an economical form of pump drive, such as an electric motor, the whole of the conditions required for operative efficiency and economy of working for a wide range of purposes appear to be complied with

The objection peculiar to surface heating in any form, viz. the slow rate of initial heating up, has been referred to, but it may be dealt with by striking a compromise between surface heating and live steam heating by admitting a limited quantity of live steam into the liquor without giving rise to serious condensation troubles

The Automatic Circulating Kier.—A further device by the authors may be referred to as effecting such a compromise, and depending for its

automatic circulation upon the suitable control and distribution of the pressure developed in the heater

The kier shown diagrammatically in fig 113A is connected at the base through a check valve C_1 to the lower receiver R The liquor pipe extends upwardly to join the upper receiver R_1 with check valves C_2, C_3, admitting respectively to pipe 3 and tubular heater The exit from the heater to the kier is by pipe 4 The pipes 5, 6, 7, 8 relate to the distribution of pressures in the respective chambers, and these relations are varied by the common valve V, which is automatically operated in accordance with the respective levels obtaining in the two receivers The effect is that, when liquor in R_1 is high and in R low, pipes 5 to 6 and 7 to 8 are respectively connected, and in the reverse state 5 to 8 and 6 to 7

The heater is supplied with steam for heating the tubes, and with a live-steam connection by means of valves V_1 and V_2 The operation is as follows Assuming the kier to be supplied with cloth and liquor, and R and heater also with liquor, float F in R is raised and F_1 in R_1 lowered, so that pipes 5 to 8 and 6 to 7 are connected Steam is turned on to V_1 and V_2, and the pressure rises in the dome of the heater, thus closing C_3 The steam passes down 6 to 7 into the receiver and empties it through 3 into R_1 R_1 exhausts its pressure through a coil in the well of the kier by 5 to 8 to C_5 The position of the floats is reversed and pipes 5 and 6, 7, and 8 are joined The steam passes through 6 to 5 to permit of the emptying of R_1 into the heater by gravity and an equivalent discharge of hot liquor enters the kier through 4 Meanwhile the kier well is draining into R and the conditions producing the reversal of the valve V occur when F and F_1 are in their extreme positions The initial operation is then repeated

The above explanation approximately describes the action occurring in the apparatus but it may be noted that initially the charges of steam detained in R and R_1 serve by condensation with the inflowing liquor to assist its motion by suction

It is at a later stage, when the temperature of liquor and steam approach equality, that these charges present a back pressure, which must be relieved, as above described

To avoid excess of steam in the well of the kier, the coil may be closed (or provided with but few perforations) and exhaust through pipe 8′ and check valve C_6 into the top of kier

In either case the pressure in the heater will tend to exceed that in the top of the kier owing to the constant evolution of steam from the liquor in contact with the heating tubes The discharge of liquor from the heater through the immersed end of pipe 4 may occur either as mentioned above, or by the pressure of the steam accumulating in the steam space above the liquor in the heater

The object of the coil in the well is to effect an exchange of heat between the discharging steam and the coolest liquor in the kier

The admission of live steam at valve V_2 is simply to augment the supply of steam which can be produced from the liquor by the heating tubes

The practical manipulation of valve V in conjunction with the operation of the floats is effected as follows —

The spindle on which each float lever is pivoted is extended into a small chamber intercepting a water-supply pipe, and the extension of the spindle is so formed as to permit or arrest the flow of water, according to the position of the lever When both levers are in either of their extreme positions a flow of water occurs for the purpose of automatically operating an oscillating lever in alternate directions by overbalancing in turn the opposite arms, on the principle of a

tipping gear This lever is connected to a piston valve, which serves the purpose of valve V In this way the motion of the floats in the receivers merely serves as a relay to control the power applied to operate the pressure regulation through valve V Thus the power required is not actually produced by the buoyancy or weight of the float Nor is the control liable to become clogged, as it is not in direct contact with the lye

The following descriptions refer more particularly to a few of the special devices adopted with the view of maintaining regular and efficient circulation —

Gebauer's Kier (*J S C I*, 1902, p 612) —The principle of this is that horizontal circulation is made use of instead of vertical

The kier consists of two concentric vessels (fig 114), one inside the other The inner, *b*, is either fixed or movable, and is perforated, as shown in the figure The outer, *a*, is placed so that spaces are left between the sides and bottoms of the two vessels

b is filled with hot lye This is drawn by means of the pump *q* from the space *h*, forced into the boiler *f*, and thence through the pipe *i* into the space between the two vessels From here it flows horizontally through the goods in the inner vessel through the pipe *d*, and back into the collecting space *h* The lye may be heated directly by steam introduced through the pipe *l*

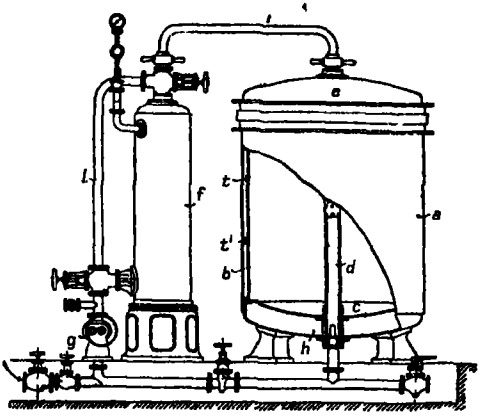


FIG 114 —Gebauer's kier

The parallel rings *t*, *t'*, projecting outwards to greater distances as they descend, cause the lye to enter the inner vessel in currents of equal force

C. J. Jackson (*J S C I*, 1901, p 712) employs a cylindrical vessel divided vertically into two compartments The outer is provided with a coil of steam pipes, and the inner connected near the bottom with two or more open low pressure kiers at a lower level Each kier is connected at the bottom by a pipe to the receiver of a centrifugal pump, connected on the discharge side with the outer compartment of the heater When the pump works the liquor is forced into the outer compartment of the heater It is here heated till it overflows into the inner, and is conducted from this to the kiers, being distributed evenly on the goods and again returning to the heater

Roesch (*J S C I*, 1902, p 342) employs two concentric cylinders The inner, holding the goods, is perforated and capable of being rotated on its axis The outer is provided with pumps on opposite sides, and the space between the two cylinders is divided into water tight compartments by projections from the inner side of the outer cylinder The liquors are forced through while the cylinder rotates, thus ensuring circulation in constantly varying directions Rotating kiers are employed for boiling rags and waste cotton

Brooks uses a number of circulation pipes, which are provided with valves capable of withstanding the pressure of a certain head of liquor When the pressure rises above this point they suddenly open and give the liquor a forward motion.

Kiers in which the Cloth is passed through the Liquor.—In all the preceding kiers the goods are stationary, while the liquor circulates We may now consider one or two examples in which the opposite conditions obtain, *i e.* the liquor remains more or less stationary, while the cloth circulates through it in the rope or open form.

Edmeston-Bentz System.—This system differs radically from the foregoing methods in that the cloth passes continuously through a special form of kier or scouring machine, wherein it is thoroughly saturated with the boiling liquor, and in this state brought into temporary contact with live steam After a further passage through the liquor it emerges and is mechanically piled down in external receptacles while still saturated, and left for an extended period to permit of the completion of the scouring process *in situ* It then proceeds to the washing, bleaching, and scouring processes in a normal manner, excepting for the introduction of automatic piling, instead of plaiting by hand labour, from the different machines, in manner similar to that shown in fig 117

The system is applicable to cloth, yarn, and warps in the rope form (see fig 115), and to cloth in the open width (fig 116) It enters and leaves the kiers through liquid seals, and is guided in a sinuous course, as shown in the accompanying illustrations, under and over rollers which guide it in its passage from one section of the machine to another The arrangements are such that the cloth can be exposed in a very thorough manner to the alternate action of the boiling liquor and steam, whereby the temperature is rapidly raised to the degree necessary to induce decomposition or solution of the impurities The liquor is maintained at the desired temperature and pressure in the kier by steam coils

The arrangement of this continuous system in the rope form is self-evident from its diagrammatic representation in fig 117, and in the case of cloth scoured in the open-width form, the method employed for the subsequent continuous washing, chemicking, and scouring with intermediate nips through squeeze rollers may be gathered from the illustration of a continuous open range in fig 118

The rate of passage of the cloth through the kier varies from 30 to 45 yards per minute, according to its weight The processes subsequent to boiling depend on whether the kier has been used with a caustic lye or milk of lime The system has been in continuous commercial operation in print- and dye-works for a number of years, and its use is extending in this connection on account of the saving in steam, labour, and the general convenience peculiar to the arrangement

Jackson Kier.—The treatment of cloth in the open width is also carried out by the more sustained boiling process employed in the kier of Messrs Jackson & Brother, of Bolton (figs 119, 120, 121)

The advantages claimed for this method are—

1 An absolutely even bleach from one end of the batch to the other

2 Selvages which have a tendency to curl are prevented from so doing, and after treatment in the kier will remain straight for subsequent processes

3 The face of the cloth is not broken

4 A better width is obtained than in rope bleaching

5 The cloth is "fuller" and less punished than in ordinary bleaching.

It is essential that the cloth should be prepared and made into good batches before going into the kier This is done on the machine illustrated in fig. 119, and is in every way effectual for its purpose It consists of a cistern from the sides of which are carried a large drum The cistern is filled with caustic liquor

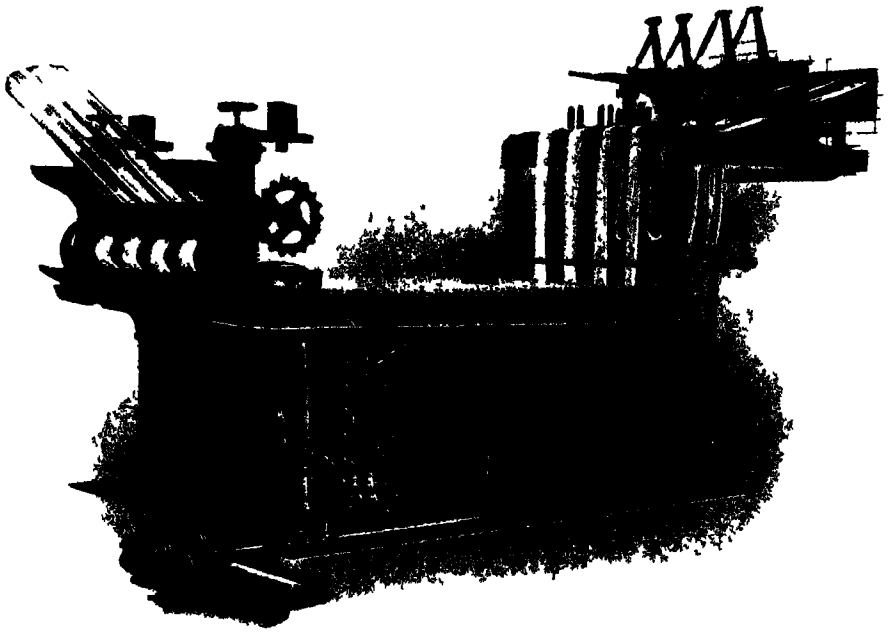


FIG 115.—Edmeston Bentz patent kier for cloth in rope form.
(A Edmeston & Sons, Ltd , Patricroft)

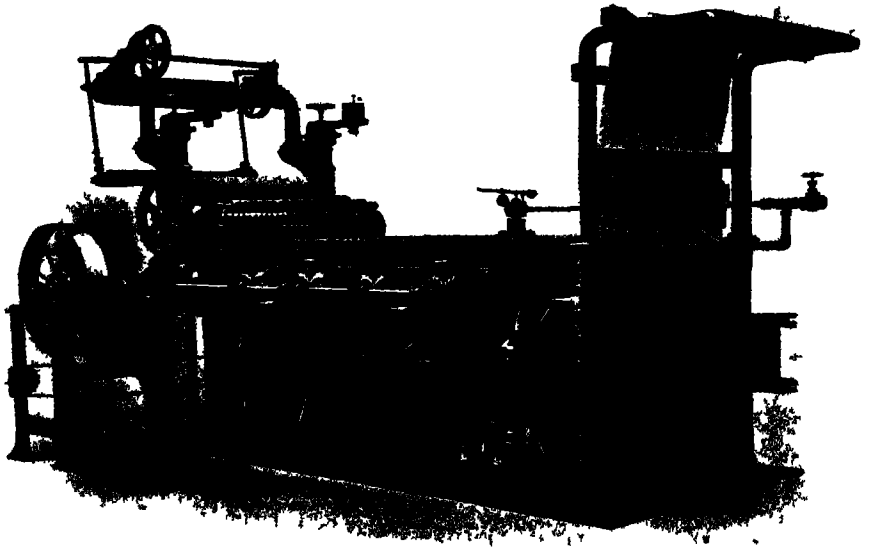


FIG. 116.—Edmeston-Bentz patent kier for cloth in open web.
(A. Edmeston & Sons, Ltd., Patricroft.)

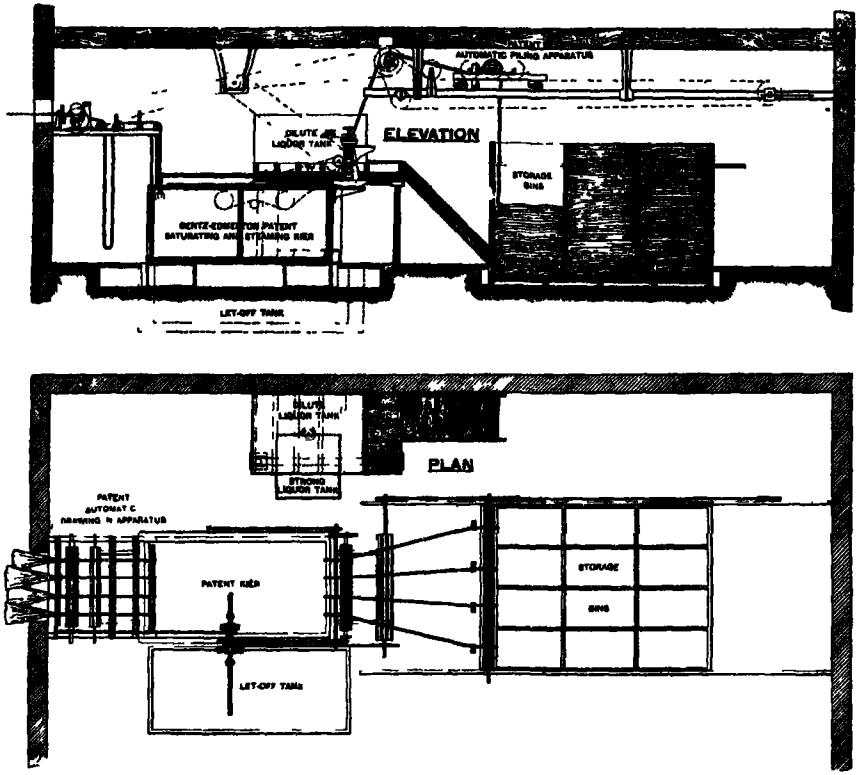


FIG. 117.—Plan and elevation of Edmeston-Bentz kier, with drawing and piling arrangement

(A. Edmeston & Sons, Ltd., Patricroft.)

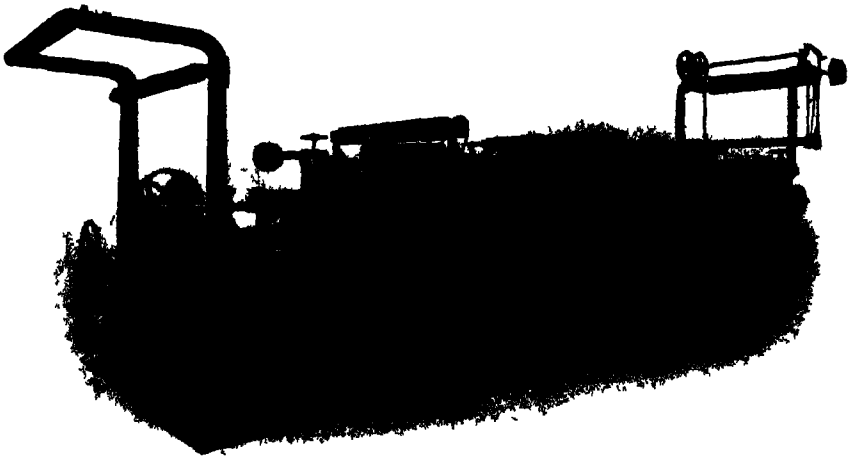


FIG. 118.—Open web chemicking, souring, and washing range

(A. Edmeston & Sons, Ltd., Patricroft.)

(which has already been used in the kier); the cloth passes round the drum and becomes thoroughly saturated. A perforated steam pipe is fixed close to the drum at bottom, and serves the purpose of heating the liquor and driving it

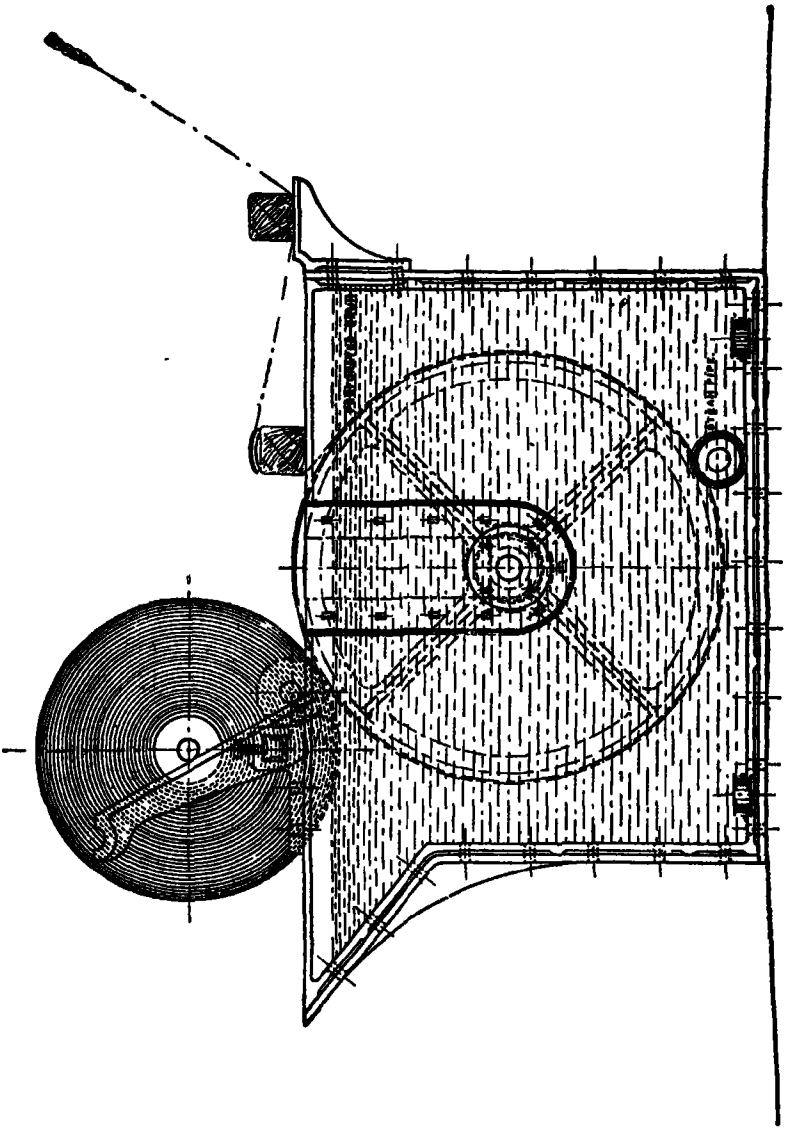


FIG. 119.—Jackson's preparing and batching machine.

through the cloth as it travels with the drum. A pair of strong batch arms are fixed on the top of the cistern and the necessary feeding rails at the front of machine.

The kier is fixed in a horizontal position, and is made of steel plates strong enough to stand a working pressure of 60 lbs. per square inch. The door is

swung on a jib crane mounted on the top of the kier, and can be easily attached and detached as required.

The cloth to be treated is made into batches on suitable batch rollers and placed in position on the wagon, which, when run into the kier, automatically couples with the driving and reversing gear at the back

The action of the drum, which lies between the two batches and remains in contact with them, notwithstanding their increasing and decreasing in size as the winding operation goes on, is fully described in fig 121, exactly the same movement being employed in this machine as in the kier.

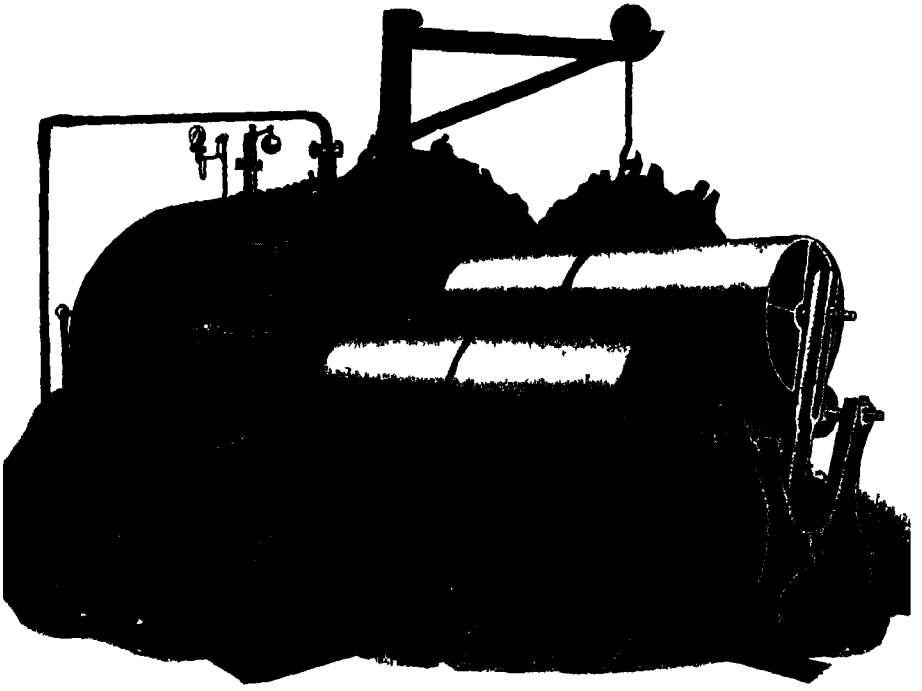


FIG 120.—Jackson's patent open bleach kier.

B1 and B2 are the two batches, which work in journals carried by the machine sides.

PD is the drum carried by the oscillating levers or arms OL These arms are free to move from side to side, being journalled at J, and the arms have an open jaw at the top; the drum PD adjusts itself to the increasing and decreasing sizes of the batches as the cloth is wound on and off This motion is most important, as it keeps the cloth always at the same tension and free from creases It also brings considerable pressure to bear on the rotating batches, and squeezes the liquor through the cloth.

The cistern sides are provided with hinged doors D for convenience of removing batches

The spurt pipes SP are used for circulating the chemic and sours by means of the pump P, and also for washing with hot or cold water when the acid or other liquor is removed from the cistern.

When the door is attached and the kier ready for work, the caustic liquor is run into the kier by means of the centrifugal pump, steam pressure is applied until a pressure of 40 lbs. is obtained, and the cloth is wound off the one batch

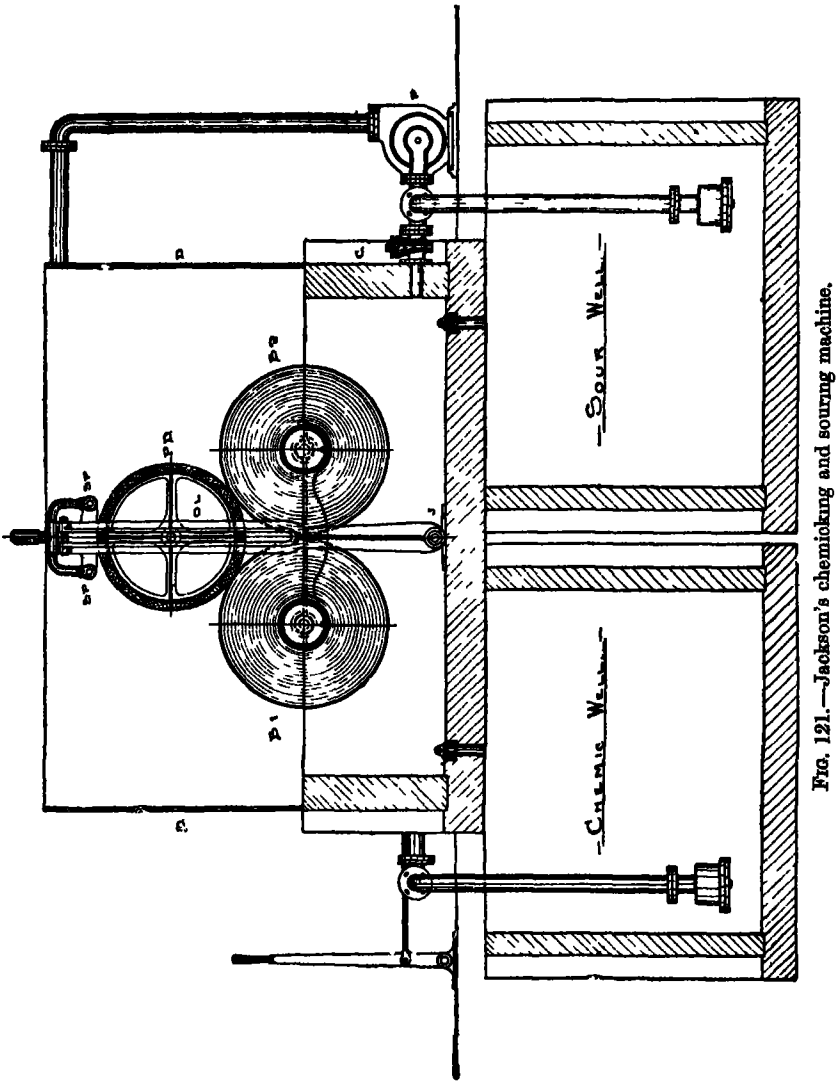


FIG. 121.—Jackson's chemicking and souring machine.

roller on to the other, and *vice versa* for two hours, at the end of which time it is thoroughly bottomed.

The reversing gear is automatic, and, after the batches are put in the kier, no attention is required until they are ready for coming out.

CHAPTER XIX.

CHEMICALS.

It will be convenient to describe briefly the chemicals mentioned already in connection with water softening and lye boiling, and to include, also, the common acids. Many of these chemicals are liable to variation and should be tested frequently.

Acids.—The chief acids used in bleaching are (1) sulphuric acid, (2) hydrochloric acid, (3) acetic acid, (4) tartaric acid. Of these, the two first named are termed "strong," while acetic and tartaric acids are, by comparison, "weak" acids. Whether an acid is a "weak" or "strong" acid depends upon the phenomenon known as "hydrogen-ion concentration" of its aqueous solutions.

Hydrogen-ion Concentration (pH Value).—The terms strong and weak have been used in speaking of acids and alkalis, and hydrogen-ion concentration has been invoked to explain why a strong acid, like hydrochloric acid, tenders cotton more readily than a weaker acid, such as acetic acid. Again, it was mentioned that the addition of sodium sulphate to sulphuric acid decreases its hydrogen-ion concentration and consequently its tendering action. Similarly, mild alkalis with a low hydroxyl-ion concentration were said to have a different action on cotton to strong alkalis with a greater hydroxyl-ion concentration. Since these terms are of considerable importance in bleaching they must be described briefly.

Water does not consist entirely of molecules represented by the formula H_2O. It is continually dissociating into its constituent ions, which are charged with equal changes of positive and negative electricity. This is represented by the equation

$$H_2O \rightleftharpoons 2H^+ + OH^-.$$

These positively and negatively charged ions are continually recombining, and, when they do, their electric charges neutralise one another. The reaction is a reversible one, as indicated by the equation given.

Thus, water consists of molecules of H_2O and free hydrogen and hydroxyl (OH) ions. Under all ordinary conditions the dissociation is very small, and there are always the same number of free positive and negative ions present, or, in other words, a constant quantity of undissociated molecules.

When this is the case a liquid is absolutely neutral. Let C_{H_2O} represent the concentration of undissociated water, and C_{H^+} the concentration of positive ions and C_{OH^-} the concentration of negative ions.

According to the law of "mass action," the rate of ion formation depends upon C_{H_2O}, and the rate of recombination upon the product $C_{H^+} \times C_{OH^-}$.

Hence $$C_{H_2O} = C_{H^+} \times C_{OH^-},$$

and $$\frac{C_{H^+} \times C_{OH^-}}{C_{H_2O}} = \text{a constant (K)}$$

or $$C_{H^+} \times C_{OH^-} = K \times C_{H_2O}.$$

This quantity $K \times C_{H_2O}$ or K_w is called the constant of dissociation for water. It has been found experimentally to be 10^{-14} This means that, in pure water, the concentration of both hydrogen and hydroxyl ions is 1 in 10,000,000. The logarithm of this number 10^{-7} is -7. Leaving out the minus, 7 is termed the pH value of water.

When hydrochloric acid is dissolved in water it dissociates, in a similar manner, into positively and negatively charged ions—

$$HCl \rightleftharpoons H^+ + Cl^-.$$

Similarly, sulphuric acid dissociates into H and SO_4 ions, and acetic into H and CH_3COO ions. The addition of an acid to water will, therefore, increase the concentration of the free hydrogen ions, or, since the product $C_H \times C_{OH}$ remains constant, diminish the concentration of the OH-ions. That is, C_H will be greater than 10^{-7}.

Similarly, when sodium hydroxide is dissolved in water, it is dissociated into Na and OH ions. Thus the concentration of OH-ions becomes greater than 10^{-7}, and consequently that of the hydrogen ions less than 10^{-7}.

From these facts, it will be seen that—

1. A solution is neutral when the concentration of both hydrogen and hydroxyl ions is 10^{-7}.

2. When the concentration of the hydrogen ions is greater than 10^{-7}, and conversely the concentration of hydroxyl ions less than 10^{-7}, a solution is acid.

3. When the concentration of the hydrogen ions is less than 10^{-7} and that of the hydroxyl ions greater than 10^{-7}, the solution is alkaline.

When equivalent weights of acids and alkalis are dissolved in water, they do not necessarily dissociate to the same extent. Thus, 1 c.c. of decinormal sulphuric acid neutralises the same weight of sodium hydroxide as 1 c.c. of acetic acid, but the hydrogen-ion concentration of the sulphuric acid is much greater than that of the acetic acid. That is, hydrogen-ion concentration is not a measure of the neutralising power of the acid, but only of its degree of acidity In common words, we say that sulphuric acid is a stronger acid than acetic, meaning that when equivalent weights of the two are dissolved in the same volume of water the strong acid has a greater hydrogen-ion concentration than the weak one. Similarly, equal volumes of decinormal solutions of sodium hydroxide and sodium carbonate will neutralise the same weight of sulphuric acid, but have, again, different hydrogen- or hydroxyl-ion concentrations. The hydroxyl-ion concentration of the sodium-hydroxide solution is greater than that of the sodium carbonate. Hence we say that the degree of alkalinity is greater, or that sodium hydroxide is a strong, and sodium carbonate a mild, alkali

The hydrogen-ion concentration in the case of acids and alkalis, compared with those of pure water, is termed the pH value.

Sörensen's Method of Expressing pH Values.—The pH value of pure water is 10^{-7}. If a solution has a hydrogen-ion concentration ten times greater than water, this would be 10×10^{-7}. If this multiplication be done by logarithms, the product of 10 multiplied by 10^{-7} is

$$\log 10 + \log 10^{-7}, \textit{ i.e. } 1 - 7, \text{ or } -6.$$

Sorensen uses the figure 6, omitting the minus sign, to express the degree of acidity of the solution (called its pH value).

The following table gives the hydrogen-ion and hydroxyl-ion concentrations corresponding to pH values from 1 to 13:—

Hydrogen-ion Concentration.	pH Value.	
$1{,}000{,}000 \times 10^{-7}$	1	Acid solutions.
$100{,}000 \times 10^{-7}$	2	
$10{,}000 \times 10^{-7}$	3	
$1{,}000 \times 10^{-7}$	4	
100×10^{-7}	5	
10×10^{-7}	6	
1×10^{-7} (water)	7	Neutral solution.
$0{\cdot}1 \times 10^{-7}$	8	Alkaline solutions.
$0{\cdot}01 \times 10^{-7}$	9	
$0{\cdot}001 \times 10^{-7}$	10	
$0{\cdot}0001 \times 10^{-7}$	11	
$0{\cdot}00001 \times 10^{-7}$	12	
$0{\cdot}000001 \times 10^{-7}$	13	

In the case of alkaline solutions the hydroxyl-ion concentrations are 10×10^{-7}, 100×10^{-7} up to $1{,}000{,}000 \times 10^{-7}$ respectively. It must be noted that, using this method of expression, the hydrogen-ion concentration decreases as the numerical value of the pH value rises, while the hydroxyl-ion concentration, on the other hand, increases. That is, a small pH value means a higher hydrogen-ion concentration than a large one.

The hydrogen-ion concentration of any particular solution of an acid in water depends upon the degree of dilution if the temperature remains constant. Thus, a normal solution of hydrochloric acid has not the same pH value as a decinormal or a centinormal solution Hence the pH values of different acids or alkalis, to be comparable, must be determined, always, on solutions containing equivalent weights, such as one molecular equivalent per litre. In the method adopted the symbol pH is the logarithm of the reciprocal of the concentration of hydrogen ions in terms of normal Thus, when pH is 2, the hydrogen-ion concentration is $N \times 10^{-2}$ or one-hundredth normal (Evers, *Analyst*, 1921, p 394)

The Determination of pH Values.—The exact measurement of pH values is very complicated and difficult Approximate values, which are sufficiently accurate for most purposes, may be determined by taking advantage of the fact that the colour changes of "indicators" only take place, as a rule, between narrow limits of hydrogen-ion or hydroxyl-ion concentration For example, sulphuric acid turns methyl orange red, but boric acid does not affect it. This is because the colour change only occurs with a hydrogen-ion concentration which is greater than that produced by a solution of boric acid. Hence, if the particular hydrogen-ion concentration at which the colour change takes place be determined by exact methods, we can obtain some information about the relative hydrogen-ion concentrations of similar solutions of sulphuric and boric acids. If a series of indicators can be found one of which changes colour at each unit of pH value, the pH value of a solution can be determined with fair accuracy by noting which indicator it affects. This is, in fact, the principle of the "colorimetric" method of finding pH values, though the indicators available overlap one another to a certain extent.

One or two examples may be given.

Indicator	Range of pH Value
Metanil yellow	1 2–2 3
Trepoeolin OO (Orange IV)	1 4–2 6
Methyl orange	2 9–4 0
Methyl red	4 2–6 3
Para-nitrophenol	5 0–7 0
Rosolic acid	6 9 8 0
Cresol red	7 2–8 8

Indicator.	Range of pH Value.
Thymol blue	8 0– 9 6
Phenol violet	8 0–10 0
Thymolphthalein	9 3–10·5
Alizarin	11 0–13 0

The colorimetric method of determination was devised by Sörensen. By mixing solutions of certain salts together with hydrochloric acid and sodium hydroxide, it is possible to prepare standards having any definite pH value.

The liquid to be tested is tried with the various indicators till one is found towards which it is approximately neutral. A series of standard mixtures is then prepared, so that some of them will have "exponents" above and others below that of the liquid to be tested The selected indicator is then added to each, and the position of the test-liquid on the scale of standards is estimated colorimetrically by comparison.

The following method of carrying out the colorimetric test is described by Evers (*Analyst*, 1921, p. 393).

There are required—

1. A complete series of indicators with well-marked colour changes covering a wide range of hydrogen-ion concentration.

2 Solutions of known hydrogen-ion concentration which are easily prepared and stable

Indicators.—The following table shows a set of indicators recommended for solutions with pH values of from 1 to 11.

Indicator	Strength of Solution	Range of pH
Thymol blue	0 04 in water	1 2–2 8 and 8 0–9 6
Bromphenol blue	0 04 „ „	2 8– 4 60
Methyl red	0 02 in 50 per cent. alcohol	4 4– 6 0
Bromcresol purple	0 04 in water	5 2– 6 8
Bromthymol blue	0 04 „ „	6 8– 8 4
Thymolphthalein	0 04 in alcohol	10 0–11 0

Standard Solutions.—It is not possible to use solutions of acids and alkalis of known strength on account of their susceptibility to changes of hydrogen-ion concentration, from such accidental causes as solubility of glass, etc. But this difficulty may be overcome by introducing certain salts, such as phosphates and borates, which act as "buffers," *i e*, when present in solution, cause the hydrogen-ion concentration to be only slightly affected by the addition of small amounts of acid and alkali.

Evers uses the following solutions :—

1 Standard N/10 sodium-citrate solution, prepared by dissolving 21·008 grammes of pure citric acid in 200 c.c. of N/10 sodium-hydroxide solution and diluting to 1000 c.c with water.

2. Standard N/5 sodium-borate solution. This is prepared by dissolving 12·404 grammes of pure boric acid in 100 c c. N/10 sodium-hydroxide solution and diluting to 1000 c.c. with water.

3 Standard M/15 potassium-dihydrogen-phosphate solution, made by dissolving 9·078 grammes of the pure salt, KH_2PO_4, in 1000 c.c. of distilled water.

4. Standard M/15 sodium-phosphate solution, prepared by dissolving 23·87 grammes of pure sodium phosphate, $Na_2HPO_4.12H_2O$, in 1000 c.c. of distilled water.

(Solutions 3 and 4 are used in combination.)

5. Standard N/10 sodium-hydroxide solution free from carbonate. This is made as follows: One hundred grammes of pure sodium hydroxide are dissolved in 100 c.c. of distilled water in a flask covered with tinfoil, and allowed to stand overnight for the carbonate to settle. The solution is then filtered quickly through a hard filter-paper with the aid of the pump. Ten c c. of the filtrate are diluted to about N/5 strength with carbon dioxide free distilled water, standardised against potassium hydrogen phthalate to phenolphthalein and diluted to N/10 strength. The solution is stored in a bottle coated with paraffin wax and connected by a glass tube to a burette. The bottle and burette have side tubes joined to soda-lime tubes to prevent the entrance of carbon dioxide.

6 Decinormal hydrochloric acid

The following tables give the proportions in which these solutions are used to give mixtures of known pH values.

pH VALUES.

0 1N Citrate Solution	0 1N HCl	pH.	0 2N Borate	0 1N HCl	pH
1 0 c c	9 0 c c	1 17	5 5 c c	4 5 c c	7 94
2 0	8 0	1 42	5 75	4 25	8 14
3 0	7 0	1 93	6 0	4 0	8 29
3 33	6 66	2 27	6 5	3 5	8 51
4 0	6 0	2 97	7 0	3 0	8 68
4 5	5 5	3 36	7 5	2 5	8 80
4 75	5 25	3 53	8 0	2 0	8 91
5 0	5 0	3 69	8 5	1 5	9 01
5 5	4 5	3·95	9 0	1 0	9 09
6 0	4 0	4 16	9 5	0 5	9 17
7 0	3 0	4 45	10 0	0 0	9 24
8 0	2 0	4 65			
9 0	1 0	4 83		0 1N NaOH	
9 5	0 5	4 89			
10 0	0 0	4 96	9 0	1 0	9 36
			8 0	2 0	9 50
	0 1N NaOH		7 0	3 0	9 68
			6 0	4 0	9 97
9 5	0 5	5 02	5 0	5 0	11·08
9 0	1 0	5 11			
8 0	2 0	5 31			
7 0	3 0	5 57			
6 0	4 0	5 97			

M/15 Na_2HPO_4.	M/15 KH_2PO_4	pH	M/15 Na_2HPO_4	M/15 KH_2PO_4.	pH
0 0 c c.	10 0 c c	4 49	6 0 c c.	4 0 c c.	6 98
0 1	9 9	4 94	7 0	3 0	7 17
0 25	9 75	5 29	8 0	2 0	7·38
0 5	9 5	5 59	9 0	1·0	7 73
1 0	9 0	5 91	9 5	0·5	8·04
2 0	8 0	6 24	9 75	0 25	8 34
3 0	7 0	6 49	9 9	0·1	8 68
4 0	6 0	6 64	10·0	0 0	9 18
5 0	5 0	6 81			

The method of determination for clear or turbid liquids free from colour is as follows: The solution is tried with the indicators until one is found which gives a tint lying between its extremes of colour. Ten c.c. of the solution are then run into a clean test-tube first washed with neutral distilled water, and 5 drops or more of the indicator are added. From the shade of colour produced the pH value can be judged approximately. Ten c.c. of a solution of this pH value are then prepared in another test-tube from the standard solutions after referring to the tables. Five drops of the indicator are added and the colours compared. If they do not match another standard is prepared.

For coloured liquids an apparatus termed a "comparator" is required. This (fig. 122) consists of a cubical block of wood bored vertically to hold four test-tubes. Two horizontal holes are also bored completely through the block, so that it is possible to look through two pairs of test-tubes simultaneously. In No. 1 hole is placed the test-tube containing 10 c c. of the solution to be tested and 5 drops of the indicator. Hole No 2, behind this, holds a tube containing 10 c.c. of distilled water. In No 3 is placed a tube containing 10 c c. of the standard solution and 5 drops of the indicator, and behind this, in No. 4, is placed a tube containing 10 c.c. of the coloured solution. In this way the colour is compensated, and the shades can be compared without interference by the colour of the solution.

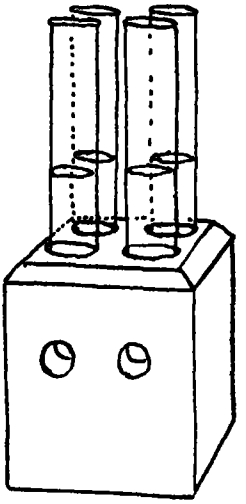


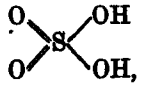
Fig 122.—Comparator set.

Mixed indicators may be used also. Thus, a "universal indicator," prepared by the British Drug Houses, Ltd, gives a range of different colours in the order of the spectrum from red to violet, each colour corresponding to a definite pH value from 3 to 11. For most purposes the values given by this indicator are sufficiently accurate. A useful comparator, together with a set of standards, is supplied also by the same firm.

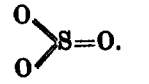
Sulphuric Acid, H_2SO_4.—Sulphuric acid is the most important of all acids. It is used not only in bleaching and dyeing, but also in the manufacture of a great many other bodies, such as hydrochloric acid, sodium sulphate, nitric acid, and a large number of other compounds both inorganic and organic It may be made by dissolving sulphur trioxide, SO_3, in water—

$$SO_3+H_2O=H_2SO_4.$$

From this reaction it appears that sulphuric acid is a compound of the acid oxide, sulphur trioxide with water, but its constitutional formula is $SO_2(OH)_2$, or



sulphur trioxide being represented by the formula



Sulphuric acid containing dissolved sulphur trioxide is made by distilling partly dehydrated ferrous sulphate. This acid, which has the formula $H_2SO_4.SO_3$,

or $H_2S_2O_7$, is termed pyrosulphuric or Nordhausen sulphuric acid. The action of heat upon ferrous sulphate is represented by the equations

$$(1)\ 6FeSO_4 = Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2.$$
$$(2)\ Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$
$$(3)\ 2SO_3 + H_2O = H_2S_2O_7.$$

Sulphuric acid, also known as oil of vitriol, is made on the large scale by the oxidation of sulphur dioxide to sulphur trioxide, and, simultaneously, dissolving the latter in water But sulphur dioxide does not combine readily with oxygen It only does so when an oxygen carrier, or catalytic agent, is present For this purpose either a little nitric acid, or finely divided platinum, is used There are two distinct processes, viz.—

1. The older chamber process, in which nitric acid is used.
2 The contact process, in which the oxidation is brought about by means of platinum.

In the chamber process, sulphur dioxide is made by burning sulphur or iron pyrites (ferrous sulphide) in air—

$$S + O_2 = SO_2,$$
$$4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3.$$

This sulphur dioxide is mixed with air (*i e* oxygen) and a little nitric acid (*i e* oxides of nitrogen) and steam, and passed into a lead chamber The sulphur dioxide is oxidised to sulphur trioxide by the aid of the nitric acid The sulphur trioxide then combines with the water-vapour present, forming sulphuric acid, which collects at the bottom of the chamber There are two or three chambers through which the mixture of gases pass, in order to give time for the reaction to be completed The acid which is formed in the chambers contains nitric acid or oxides of nitrogen This acid (known as chamber acid) must be freed from these impurities Moreover, the air which leaves the chamber contains, also, oxides of nitrogen, which must be recovered This is done by means of the Gay Lussac tower This is a tall chamber packed with flints or coke. The gases from the chamber pass up it from bottom to top As they rise through the coke, they meet a descending stream of pure sulphuric acid This dissolves the oxides of nitrogen, or nitric acid vapour, and the descending acid is collected at the bottom of the tower This acid, together with the chamber acid, is now pumped to the top of another tower, the Glover tower, constructed like the Gay-Lussac tower As it trickles down this tower, it meets the hot gases from the sulphur or pyrites oven. The oxides of nitrogen which the acid contains are taken up by the ascending gases and carried on to the chamber. The acid which collects at the bottom of the tower is free from nitric acid, and has been somewhat concentrated, also, by the hot gases from the ovens *It contains from 60 to 70 per cent. of sulphuric acid, and is concentrated* in either lead or silica pans according to the quality of the acid required The nitric acid acts as a catalytic agent, *i e.* it is recovered unchanged at the end of the reactions and is used again. It is probable that, first of all, nitrous acid is formed, which is then changed into nitrosyl-sulphuric acid, $SO_2(ONO)OH$—

$$2SO_2 + 2HNO_2 + O_2 = 2SO_2(ONO)OH.$$

This nitrosyl-sulphuric acid is then decomposed by water with the formation of sulphuric and nitrous acids—

$$2SO_2(ONO)OH + 2H_2O = 2H_2SO_4 + 2HNO_2.$$

Nitrosyl-sulphuric acid forms what are known as "chamber crystals," which are deposited on the sides of the chambers if there is not enough water vapour present to decompose them In the contact process, a mixture of sulphur dioxide and air is passed over platinised asbestos contained in perforated tubes in a chamber The mixed gases pass through this asbestos when the reaction $2SO_2+O_2=2SO_3$ takes place, under the influence of the finely divided platinum The sulphur trioxide is condensed in concentrated sulphuric acid and forms Nordhausen acid But, if the acid is diluted with water, sulphuric acid is obtained—

$$H_2S_2O_7+H_2O=2H_2SO_4$$

The temperature of the asbestos is kept at about 400° C If it is much higher, the sulphur trioxide is decomposed into sulphur dioxide and oxygen, while if the temperature is too low, the reaction is incomplete and sulphur dioxide is lost

Commercial sulphuric acid is of two kinds, known as "brown oil of vitriol" or dark oil of vitriol (BOV and DOV), and "oil of vitriol" (OV)

The brown oil of vitriol owes its colour to impurities such as charred organic matter It contains also lead and other salts and sometimes nitric acid Arsenious oxide is also generally present Lead is always present in sulphuric acid which has been concentrated in lead pans above a strength of 79 per cent Up to this concentration sulphuric acid does not attack lead After concentrating to 79 per cent of sulphuric acid, therefore, the evaporation is continued in quartz or platinum retorts Oil of vitriol (OV) is free from colour When crude sulphuric acid is heated, water is lost till the mixture contains 98·3 per cent. of sulphuric acid, when the acid distils unchanged Thus, sulphuric acid purified by distillation contains 98 3 per cent of real acid, H_2SO_4 Distillation frees it from all its impurities except arsenic Absolute sulphuric acid, H_2SO_4, can be obtained as crystals by freezing the 98 3 per cent solution, or by adding sufficient sulphur trioxide to combine with the water present These melt at 10 5° C forming pure sulphuric acid

Properties of Sulphuric Acid.—Sulphuric acid (OV) is a colourless, syrupy liquid, with a specific gravity of 1 84 at 15° C It boils at 338° C, the distillate containing 98 3 per cent of acid When heated to 440° C it decomposes, forming sulphur dioxide and water Sulphuric acid dissolves in water in all proportions When it is mixed with water, heat is evolved, and, on cooling, the solution contracts This evolution of heat during solution, followed by contraction on cooling, indicates that a chemical change has taken place—that is, that the water and sulphuric acid have combined There are, in fact, three different hydrates of sulphur trioxide (1) H_2SO_4, (2) $H_2SO_4\,H_2O$, (3) $H_2SO_4\,2H_2O$ The maximum contraction takes place when sulphuric acid and water are mixed in the proportions represented by the formula $H_2SO_4\,2H_2O$

The affinity of sulphuric acid for water is shown by other reactions It attracts moisture from the air very readily When brought into contact with carbohydrates, it decomposes them, withdrawing the hydrogen and oxygen and leaving carbon Thus

$$C_6(H_2O)_6+3H_2SO_4=6C+3H_2SO_4\,6H_2O$$

Sulphuric acid is used for carbonising wool to remove cellulose on account of its action on carbohydrates When alcohol is treated with sulphuric acid, ethylene gas, C_2H_4, is formed—

$$C_2H_6O=H_2O+C_2H_4\,,$$

or, if formic acid be heated with sulphuric acid, carbon monoxide is produced—

$$HCOOH = H_2O + CO.$$

Sulphuric acid dissolves and decomposes many other organic substances, such as skin and wool and cotton.

The special action of sulphuric acid on cotton is described in Chapter IX.

Sulphuric acid is a "strong" acid, *i.e.* it has a high hydrogen-ion concentration. It turns methyl orange or blue litmus red.

Its aqueous solution has a sour taste, and neutralises bases or dissolves many metals to form salts. Its action on metals is peculiar in some respects. It dissolves some, such as iron and zinc, with the formation of a sulphate of the metal and liberation of hydrogen—

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

But in these cases water must also be present. The sulphates are not soluble in concentrated sulphuric acid, and soon form a layer which protects the metal from the further action of the acid. When zinc is placed in concentrated sulphuric acid it is attacked at first, but the action soon ceases. If, now, water be added, a rapid effervescence sets in and the metal is completely dissolved.

Some metals, such as copper, are not readily soluble in cold sulphuric acid, but dissolve when the acid is heated with the evolution of sulphur dioxide. This is due to the reduction of some of the sulphuric acid by the hydrogen which is produced first The solution takes place in three stages :

(1) $Cu + H_2SO_4 = CuSO_4 + H_2$
(2) $H_2SO_4 + H_2 = H_2SO_3 + H_2O.$
(3) $H_2SO_3 = SO_2 + H_2O.$

Sulphuric acid is dibasic, *i e* contains two atoms of hydrogen replaceable by metals, forming both normal and acid salts. The sulphates are prepared either by treating the metal, its oxide or carbonate, with sulphuric acid, or, in some cases, by double reaction Sodium sulphate is made, also, as a by-product in the manufacture of hydrochloric acid.

The sulphates are, as a rule, crystalline compounds which are soluble in water They contain generally water of crystallisation Many sulphates occur in nature. Among these are—

Epsom Salt	$MgSO_4\,7H_2O.$
Kainite	$K_2SO_4\,MgSO_4\,6H_2O$
Gypsum	$CaSO_4\,2H_2O$
Barytes	$BaSO_4$

Some of the sulphates are made use of in cotton finishing, and will be described in Chapter XXIX.

Analysis of Sulphuric Acid.—The strength of a sample of sulphuric acid may be found by taking its specific gravity and referring to a table of specific gravities.

For technical purposes the Twaddell hydrometer is generally used for the determination of specific gravities. This is graduated upon an arbitrary scale. In order to obtain true specific gravities the number of degrees Twaddell are multiplied by 5 and the product added to 1000. Thus, a liquid indicating a density of 5° Tw. would have a specific gravity of $5 \times 5 + 1000$, *i.e.* 1025. Conversely, specific gravities are converted into degrees Twaddell by subtracting 1000 and dividing the remainder by 5.

When using a hydrometer, it must be remembered that it only gives accurate

readings at the temperature at which it was graduated, viz. 15° C. The temperature of the liquid must, therefore, be adjusted carefully.

The Baumé hydrometer is used occasionally, but its readings are difficult to translate into specific gravities. The factor is

$$\frac{14000}{130 \times \text{degrees Bé}} = \text{specific gravity.}$$

The following tables give the relations between thermometric scales, specific gravities, and the corresponding percentages of sulphuric acid.—

COMPARISON OF DIFFERENT THERMOMETRIC SCALES.

Cent.	Réaum.	Fahr.	Cent.	Réaum.	Fahr.	Cent.	Réaum.	Fahr.
−40	−32·0	−40 0	+ 7	+5·6	+44·6	+54	+43 2	+129·2
39	31·2	38·2	8	6·4	46·4	55	44·0	131·0
38	30·4	36·4	9	7 2	48 2	56	44·8	132·8
37	29·6	34 6	10	8·0	50 0	57	45·6	134 6
36	28·8	32·8	11	8·8	51 8	58	46·4	136·4
35	28 0	31·0	12	9·6	53 6	59	47·2	138·2
34	27 2	29 2	13	10 4	55·4	60	48 0	140 0
33	26·4	27 4	14	11 2	57·2	61	48 8	141·8
32	25 6	25 6	15	12·0	59 0	62	49·6	143 6
31	24·8	23·8	16	12 8	60·8	63	50 4	145·4
30	24 0	22·0	17	13 6	62 6	64	51·2	147 2
29	23·2	20·2	18	14 4	64 4	65	52·0	149 0
28	22·4	18 4	19	15 2	66·2	66	52·8	150·8
27	21 6	16·6	20	16 0	68 0	67	53 6	152·6
26	20 8	14·8	21	16 8	69·8	68	54·4	154·4
25	20·0	13·0	22	17·6	71 6	69	55·2	156 2
24	19 2	11·2	23	18 4	73·4	70	56·0	158·0
23	18 4	9·4	24	19 2	75·2	71	56·8	159·8
22	17·6	7·6	25	20·0	77 0	72	57·6	161·6
21	16 8	5·8	26	20·8	78 8	73	58·4	163·4
20	16·0	4·0	27	21·6	80 6	74	59·2	165·2
19	15·2	2·2	28	22 4	82 4	75	60·0	167 0
18	14·4	0 4	29	23·2	84 2	76	60 8	168·8
17	13 6	+1·4	30	24·0	86·0	77	61·6	170·6
16	12 8	3 2	31	24·8	87·8	78	62·4	172·4
15	12·0	5·0	32	25 6	89 6	79	63·2	174·2
14	11·2	6·8	33	26·4	91·4	80	64·0	176·0
13	10·4	8·6	34	27 2	93·2	81	64·8	177·8
12	9·6	10·4	35	28 0	95·0	82	65·6	179·6
11	8·8	12·2	36	28·8	96 8	83	66·4	181·4
10	8·0	14·0	37	29·6	98·6	84	67·2	183 2
9	7·2	15 8	38	30 4	100 4	85	68 0	185·0
8	6·4	17·6	39	31·2	102·2	86	68·8	186 8
7	5·6	19·4	40	32 0	104 0	87	69 6	188 6
6	4·8	21·2	41	32 8	105·8	88	70 4	190 4
5	4·0	23·0	42	33 6	107 6	89	71·2	192·2
4	3 2	24·8	43	34·4	109 4	90	72 0	194 0
3	2·4	26·6	44	35·2	111·2	91	72·8	195 8
2	1·6	28·4	45	36·0	113·0	92	73 6	197 6
1	0·8	30·2	46	36·8	114·8	93	74 4	199 4
0	0·0	32·0	47	37·6	116·6	94	75 2	201·2
+1	+0 8	33·8	48	38·4	118 4	95	76·0	203 0
2	1·6	35·6	49	39·2	120 2	96	76·8	204·8
3	2·4	37·4	50	40·0	122·0	97	77·6	206·6
4	3·2	39·2	51	40 8	123·8	98	78·4	208·4
5	4·0	41·0	52	41 6	125·6	99	79·2	210·2
6	4·8	42·8	53	42·4	127·4	100	80·0	212·0

COMPARISON OF THE HYDROMETER DEGREES ACCORDING TO BAUMÉ AND TWADDELL WITH THE SPECIFIC GRAVITIES.

Baumé	Twaddell.	Specific Gravity	Baumé	Twaddell.	Specific Gravity	Baumé.	Twaddell.	Specific Gravity.
0	0	1 000	19·3	31	1 155	36 0	66 4	1 332
0·7	1	1 005	19 8	32	1·160	36 2	67	1 335
1 0	1·4	1 007	20 0	32·4	1·162	36·6	68	1·340
1·4	2	1 010	20 3	33	1·165	37 0	69	1·345
2·0	2 8	1·014	20 9	34	1·170	37 4	70	1 350
2·1	3	1 015	21 0	34 2	1 171	37 8	71	1·355
2·7	4	1·020	21 4	35	1·175	38 0	71·4	1·357
3 0	4 4	1 022	22·0	36	1 180	38 2	72	1·360
3 4	5	1 025	22 5	37	1 185	38 6	73	1 365
4 0	5 8	1·029	23 0	38	1 190	39 0	74	1 370
4·1	6	1·030	23·5	39	1 195	39 4	75	1·375
4 7	7	1 035	24 0	40	1 200	39 8	76	1·380
5 0	7·4	1·037	24 5	41	1 205	40·0	76 6	1 383
5 4	8	1 040	25 0	42	1 210	40 1	77	1 387
6 0	9	1 045	25 5	43	1 215	40 5	78	1·390
6·7	10	1 050	26 0	44	1·220	40 8	79	1 395
7 0	10·2	1 051	26 4	45	1·225	41 0	79 4	1 397
7·4	11	1 055	26 9	46	1 230	41 2	80	1·400
8 0	12	1 060	27 0	46 2	1·231	41 6	81	1 405
8·7	13	1 065	27 4	47	1 235	42 0	82	1·410
9 0	13·4	1 067	27 9	48	1·240	42·3	83	1·415
9 4	14	1 070	28 0	48 2	1·241	42 7	84	1 420
10 0	15	1 075	28 4	49	1 245	43·0	84 8	1·424
10 6	16	1 080	28 8	50	1 250	43 1	85	1 425
11 0	16 6	1·083	29 0	50 4	1 252	43 4	86	1·430
11 2	17	1 085	29·3	51	1 255	43 8	87	1 435
11·9	18	1 090	29·7	52	1·260	44·0	87 6	1 438
12 0	18 2	1·091	30·0	52·6	1 263	44 1	88	1 440
12 4	19	1 095	30 2	53	1·265	44 4	89	1·445
13 0	20	1·100	30 6	54	1·270	44 8	90	1 450
13·6	21	1·105	31 0	54 8	1·274	45 0	90 6	1 453
14 0	21 6	1 108	31·1	55	1 275	45 1	91	1·455
14 2	22	1 110	31 5	56	1 280	45 4	92	1 460
14 9	23	1 115	32 0	57	1 285	45 8	93	1 465
15 0	23 2	1 116	32 4	58	1 290	46 0	93 6	1 468
15·4	24	1·120	32 8	59	1 295	46 1	94	1 470
16 0	25	1·125	33·0	59 4	1 297	46 4	95	1 475
16 5	26	1 130	33 3	60	1 300	46 8	96	1 480
17 0	26·8	1 134	33·7	61	1·305	47 0	96 6	1 483
17·1	27	1·135	34·0	61 6	1 308	47 1	97	1 485
17 7	28	1 140	34·2	62	1·310	47·4	98	1 490
18 0	28 4	1 142	34·6	63	1 315	47 8	99	1 495
18·3	29	1 145	35 0	64	1 320	48 0	99 6	1 498
18·8	30	1 150	35·4	65	1 325	48 1	100	1 500
19 0	30 4	1 152	35 8	66	1·330	48 4	101	1 505

Sulphuric Acid.

	Sp. gr.	Tw.°	Per cent H_2SO_4	Weight of 1 cu ft in lbs Av	Per cent O. V.	Pounds O. V in 1 cu ft.	°Freezing (Melting) Point
0	1 0000	0·0	0 00	62 37	0 00	0 00	32 0° F
1	1 0069	1 4	1 02	62 80	1 09	0 68	31 2 ,,
2	1 0140	2 8	2 06	63 24	2 22	1 41	30 5 ,,
3	1 0211	4 2	3 13	63 69	3 36	2 14	29 8 ,,
4	1 0284	5 7	4 21	64 14	4 52	2 90	28 9 ,,
5	1 0357	7 1	5 28	64 60	5 67	3 66	28 1 ,,
6	1 0432	8 6	6 37	65 06	6 84	4 45	27 2 ,,
7	1 0509	10 1	7 45	65 53	7 99	5 24	26 3 ,,
8	1 0584	11 7	8 55	66 01	9 17	6 06	25 1 ,,
9	1 0662	13 2	9 66	66 50	10 37	6 89	24 0 ,,
10	1 0741	14 8	10 77	66 99	11 56	7 74	32 8 ,,
11	1 0821	16 4	11 89	67 49	12 76	8 61	21 5 ,,
12	1 0902	18 0	13 01	68 00	13 96	9 49	20 0 ,,
13	1 0985	19 7	14 13	68 51	15 16	10 39	18 3 ,,
14	1 1069	21 4	15 25	69 04	16 38	11 30	16 6 ,,
15	1 1154	23 1	16 38	69 57	17 58	12 23	14 7 ,,
16	1 1240	24 8	17 53	70 10	18 81	13 19	12 6 ,,
17	1 1328	26 6	18 71	70 65	20 08	14 18	10 2 ,,
18	1 1417	28 3	19 89	71 21	21 34	15 20	7 7 ,,
19	1 1508	30 2	21 07	71 78	22 61	16 23	4 8 ,,
20	1 1600	32 0	22 25	72 35	23 87	17 27	1 6 ,,
21	1 1694	33 9	23 43	72 94	25 14	18 34	- 1 8 ,,
22	1 1789	35 8	24 61	73 53	26 41	19 42	- 6 0 ,,
23	1 1885	37 7	25 81	74 13	27 69	20 53	-11 ,,
24	1 1983	39 7	27 03	74 74	29 00	21 68	-16 ,,
25	1 2083	41 7	28 28	75 36	30 34	22 87	-22 ,,
26	1 185	43 7	29 53	76 00	31 69	24 08	-30 ,,
27	1 2288	45 8	30 79	76 64	33 04	25 32	-39 ,,
28	1 2393	47 9	32 05	77 30	34 39	26 58	-49 ,,
29	1 2500	50 0	33 33	77 96	35 76	27 88	-61 ,,
30	1 2609	52 2	34 63	78 64	37 16	29 22	-74 ,,
31	1 2719	54 4	35 93	79 33	38 55	30 58	-82 ,,
32	1 2832	56 6	37 26	80 03	39 98	32 00	-96 ,,
33	1 2946	58 9	38 58	80 74	41 40	33 42	-97 ,,
34	1 3063	61 3	39 92	81 47	42 83	34 90	-91 ,,
35	1 3182	63 6	41 27	82 22	44 28	36 41	81 ,,
36	1 3303	66 1	42 63	82 97	45 74	37 95	70 ,,
37	1 3426	68 5	43 99	83 74	47 20	39 53	-10 ,,
38	1 3551	71 0	45 35	84 52	48 66	41 13	-53 ,,
39	1 3679	73 6	46 72	85 32	50 13	42 77	-47 ,,
40	1 3810	76 2	48 10	86 13	51 61	44 45	41 ,,
41	1 3942	78 8	49 47	86 96	53 08	46 16	-35 ,,
42	1 4078	81 6	50 87	87 80	54 58	47 92	-31 ,,
43	1 4216	84 3	52 26	88 67	56 07	49 72	-27 ,,
44	1 4356	87 1	53 60	89 54	57 58	51 56	-23 ,,
45	1 4500	90 0	55 07	90 44	59 09	53 44	-20 ,,
46	1 4646	92 9	56 48	91 35	60 60	55 36	-14 ,,
47	1 4796	95 9	57 90	92 28	62 13	57 33	15 ,,
48	1 4948	99 0	59 33	93 23	63 65	59 34	-18 ,,
49	1 5104	102 1	60 75	94 20	65 18	61 40	22 ,,
50	1 5263	105 3	62 18	95 20	66 72	63 52	-27 ,,
51	1 5426	108 5	63 66	96 21	68 31	65 72	-33 ,,
52	1 5591	111 8	65 13	97 24	69 89	67 96	-39 ,,
53	1 5761	115 2	66 64	98 30	71 50	70 28	-49 ,,
54	1 5934	118 7	68 13	99 38	73 11	72 66	-59 ,,
55	1 6111	122 2	69 65	100 48	74 74	75 10	Below -40
56	1 6292	125 8	71 17	101 61	76 37	77 60	
57	1 6477	129 5	72 75	102 77	78 07	80 23	
58	1 6667	133 3	74 36	103 95	79 79	82 95	
59	1 6860	137 2	75 99	105 16	81 54	85 75	-7
60	1 7059	141 2	77 67	106 40	83 35	88 68	+12 6° F
61	1 7262	145 3	79 43	107 66	85 23	91 76	27 3 ,,
62	1 7470	149 4	81 30	108 96	87 24	95 06	39 1 ,,
63	1 7683	153 7	83 34	110 29	89 43	98 63	46 1 ,,
64	1 7901	158 0	85 66	111 65	91 92	102 68	49 4 ,,
64½	1 7957	159 1	86 33	112 00	92 64	103 75	48 6 ,,
64⅔	1 8012	160 2	87 04	112 34	93 40	104 93	41 1 ,,
64¾	1 8068	161 4	87 81	112 69	94 23	106 19	37 9 ,,
65	1 8125	162 5	88 66	113 05	95 13	107 54	33 1 ,,
65¼	1 8182	163 6	89 55	113 40	96 10	108 97	24 6 ,,
65½	1 8239	164 8	90 60	113 76	97 22	110 60	13 4 ,,
65¾	1 8297	165 9	91 80	114 13	98 51	112 42	- 1 ,,
66	1 8354	167 1	93 19	114 47	100 00	114 47	-29 ,,

APPROXIMATE BOILING POINTS.

50° Bé	295° F.
60° ,,	386° ,,
61° ,,	400° ,,
62° ,,	415° ,,
63° ,,	432° ,,
64° ,,	451° ,,
65° ,,	480° ,,
66° ,,	538° ,,

FIXED POINTS

Sp gr	Per cent H_2SO_4	Sp gr	Per cent H_2SO_4
1 0000	0 00	1 5231	62 34
1 0048	0 71	1 5440	63 79
1 0347	5 14	1 5748	66 51
1 0640	9 48	1 5972	71 00
1 0992	14 22	1 6679	74 46
1 1453	19 04	1 7044	77 54
1 1736	23 94	1 7258	79 40
1 2105	28 65	1 7472	81 32
1 2513	33 49	1 7700	83 47
1 2961	38 64	1 7959	86 36
1 3441	44 15	1 8117	88 53
1 3947	49 52	1 8194	89 75
1 4307	53 17	1 8275	91 32
1 4667	56 68	1 8364	93 19
1 4822	58 14		

ALLOWANCE FOR TEMPERATURE

At 10° Bé	0 029° Bé	or 0 00023 sp gr	= 1° F.
,, 20° ,,	0 036° ,,	0 00034 ,,	= 1° ,,
,, 30° ,,	0 035° ,,	0 00049 ,,	= 1° ,,
,, 40° ,,	0 031° ,,	0 00041 ,,	= 1° ,,
,, 50° ,,	0 028° ,,	0 00045 ,,	= 1° ,,
,, 60° ,,	0 026° ,,	0 00053 ,,	= 1° ,,
,, 63° ,,	0 026° ,,	0 00057 ,,	= 1° ,,
,, 66° ,,	0 0235° ,,	0 00054 ,,	= 1° ,,

Per cent 60°	Pounds 60° in 1 cu ft	Per cent 50°	Pounds 50° in 1 cu ft
61 93	53 34	77 38	60 62
63 69	55 30	79 58	62 19
65 50	57 50	81 81	71 83
67 23	59 06	84 05	74 58
69 09	61 86	86 30	77 27
70 90	64 12	88 58	80 10
72 72	66 43	90 83	82 98
74 55	68 79	93 12	85 93
76 37	71 20	95 40	88 94
78 22	73 68	97 70	92 03
80 06	76 21	100 00	95 20
81 96	78 85	102 38	98 50
83 86	81 54	104 74	101 85
85 79	84 33	107 15	105 33
87 72	87 17	109 57	108 89
89 67	90 10	112 01	112 55
91 63	93 11	114 46	116 30
93 67	96 26	117 00	120 24
95 74	99 52	119 59	124 31
97 84	102 89	122 21	128 52
100 00	106 40	1 4 91	132 91
102 27	110 10	127 74	137 52
104 57	114 05	130 75	142 47
107 30	118 34	134 03	147 82
110 29	123 14	137 76	153 81
111 15	1 4 49	138 84	155 50
112 06	125 89	139 98	157 25
113 05	127 40	141 22	159 14
114 14	129 03	142 57	161 17
115 30	130 75	144 02	163 32
116 65	132 70	145 71	165 76
118 19	134 88	147 63	168 48
119 98	137 34	149 87	171 56

	H_2SO_4.	O V	60°
O. V	93 19	100 00	119 98
60°	77 67	83 35	100 00
50°	62 18	66 72	80 06

Acids stronger than 66° Bé should have their percentage compositions determined by chemical analysis.

* Calculated from Pickering's results, *Journal of Chemical Society*, vol lvii p. 863.

Hydrometers.—A hydrometer (fig. 123) is constructed of glass. Its lower end is weighted with mercury, in order to make the instrument sink to a convenient depth and preserve an upright position The cylindrical stem is graduated, the divisions corresponding to specific gravities When a hydrometer is placed in a liquid, it sinks until the weight of the liquid displaced is equal to that of the hydrometer Thus, it is evident that the less the specific gravity of the liquid, the deeper will the instrument sink in it. Hence, if a uniform system of graduation be adopted, so that all instruments give the same readings in liquids of the same specific gravities, the density of a liquid can be obtained by immersing a hydrometer in it and noting the depth to which it sinks.



Fig 123 —Hydrometer

In Twaddell's hydrometer the graduations are placed at distances from one another corresponding to equal differences in density.

When using a hydrometer the containing vessel must be wide enough for the instrument to float freely without touching the sides.

Specific gravities may be determined rather more accurately by means of a Westphal hydrostatic balance (fig. 124).

This is an instrument which indicates the specific gravity of a liquid by the relative loss of weight of a plummet of known volume when suspended in the liquid. The apparatus comprises a balance, a glass plummet which is commonly provided with a thermometric scale, a cylinder to contain the liquid to be tested, and two sets of weights in the form of riders which can be suspended on the graduated beam of the balance. The heaviest rider has exactly the same weight as that of the water displaced by the plummet at 15° C. The remaining riders weigh successively $\frac{1}{10}$th, $\frac{1}{100}$th, and $\frac{1}{1000}$th of the first. The balance must be protected from draughts when used. It is adjusted, by means of the screw at its foot, so that when the beam is oscillating, with the plummet suspended from the hook at the end, the pointer at the other end comes to rest exactly opposite the other pointer on the curved arm on the stand The cylinder is next filled with the liquid, at a temperature of 15° C, and the pointer is then brought back to the zero position by suspending the riders on the graduated beam. If the specific gravity of the liquid is 1·0, this will be done by suspending the heaviest rider on the same hook as the plummet If equilibrium is produced when it is suspended at division 9 on the scale, the specific gravity is 0·9 If the specific gravity is greater than 1·0, having suspended the first heaviest rider at division 10, the second place of decimals is found by placing the second at some intermediate point Similarly, the third and fourth decimals are found by means of the lighter riders Finally, the specific gravity is read off from the riders and their position on the scale

The determination of the strength of a solution from its specific gravity is only reliable for pure substances If other soluble bodies are present, they will, naturally, affect the specific gravity of the solution and be returned as the substance itself.

For accurate determinations the following method should be employed: A small quantity (about 5 grammes) of the acid is weighed in a stoppered weighing bottle and washed into a 250 c c. flask with distilled water. After cooling, the contents of the flask are made up to 250 c c. and well mixed. An aliquot part, *e.g.* 50 c.c., is then withdrawn and titrated with normal sodium hydroxide, with

methyl orange as indicator. Each cubic centimetre of normal alkali neutralises 0·049 gramme of sulphuric acid. The chief impurities of sulphuric acid are lead sulphate, iron sulphate, and nitric acid. Sodium sulphate may also be present, and sulphuric acid made from iron pyrites always contains arsenic. Lead sulphate may be detected by diluting the sample with water and letting the mixture stand, when insoluble lead sulphate will settle down. It may be estimated by filtering it off on a weighed Gooch crucible, washing with 1 per cent sulphuric acid, igniting gently and weighing. Lead sulphate, compounds of iron, or sodium sulphate remain when a small quantity of the acid is heated in a dish till all the sulphuric acid is expelled. The residue may be weighed. In a good sample of commercial acid it is very small, while in pure acid it is *nil*. Iron in this residue may be detected and estimated colorimetrically in the manner described for water. Nitric acid or oxides of nitrogen may be detected by

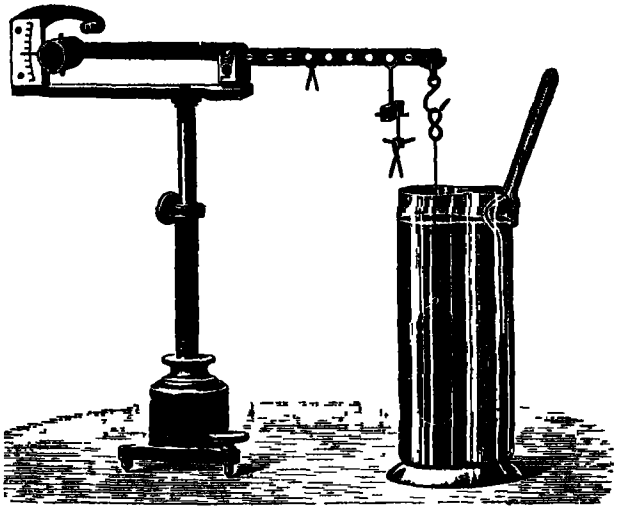


Fig. 124.—Westphal hydrostatic balance

means of the brown ring or diphenylamine tests. If a dilute solution of ferrous sulphate be poured on to the surface of some of the strong acid in a test-tube, so that it floats on the surface, a brown ring is formed at the junction of the two liquids if nitric acid is present. This is caused by the formation of nitric oxide, which dissolves in the ferrous sulphate solution—

$$6FeSO_4+3H_2SO_4+2HNO_3=3Fe_2(SO_4)_3+4H_2O+2NO.$$

The diphenylamine test is more delicate. A small quantity of the reagent is dissolved in pure sulphuric acid and the solution added to some of the acid to be tested. If nitric acid be present an intense blue colour is produced. Nitric acid may be estimated by several methods.

The nitrometer method depends upon the fact that when nitric acid is shaken with metallic mercury in the presence of sulphuric acid, nitric oxide is produced—

$$2HNO_3+3H_2SO_4+3Hg=3HgSO_4+2NO+4H_2O.$$

A nitrometer (fig. 125) is filled with clean mercury. Five c.c., or a known

weight, of the strong sulphuric acid are placed in the cup (f), and allowed to enter the nitrometer by careful manipulation of the three-way tap, taking care that no air is included. The graduated tube (a) of the nitrometer is then taken in the right hand and, resting it on the left, is depressed to an angle of from 45° to 60°, at the same time bringing the liquid into contact with the mercury by a rotatory movement of the right hand. The upper portion of the mercury should be broken up into small globules for reduction of the nitrate to take place. This agitation is continued till no increase in the volume of gas liberated can be observed. The tube is then replaced in the stand and the nitric oxide brought to atmospheric temperature The level of the mercury in the open tube (b) is adjusted till the gas is under atmospheric pressure, its volume read off and corrected for temperature and pressure For example, 5 c c of sulphuric acid gave 3·3 c c. of nitric oxide The atmospheric pressure was 766 mm. and temperature 20° C Hence the volume at 0° C. and 760 mm pressure is

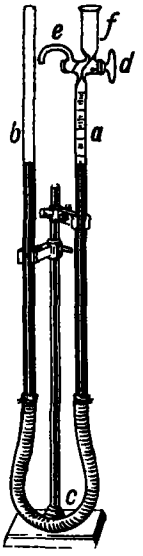


Fig 125 — Nitrometer

$$\frac{3{\cdot}3\times273\times766}{293\times760}.$$

One c c. of nitric oxide at 0° C. and 760 mm. pressure contains 0·000625 gramme of nitrogen or 0·00282 gramme of nitric acid.

A simpler method is to reduce the nitric acid to ammonia and estimate this by distilling it into decinormal acid and titrating Five c.c. of the acid are placed in a flask, diluted to about 50 c.c with water, and 5 grammes of reduced iron are added. When effervescence has ceased, the ammonia produced by the reduction of the nitric acid (present as ammonium sulphate) is estimated in the same way as in the Kjeldahl process The indigo-carmine process is also very simple and rapid. Five grammes of indigo carmine are made into a paste with water and dissolved in 1 litre of 5 per cent sulphuric acid A standard solution of potassium nitrate containing 0·722 gramme per litre is also prepared (1 c c. 0·001 gramme nitrogen). The indigo-carmine solution is then standardised by placing 5 c.c of the nitrate solution in a beaker or dish, warming, and running in the indigo carmine from a burette with constant stirring till the blue colour is just permanent From the volume used the amount of nitric acid equivalent to each cubic centimetre solution can be determined. Five c c , or a known weight, of the sulphuric acid are then placed in the dish, diluted with water, and titrated in the same way

Hydrochloric acid, HCl, which is a gas at ordinary temperatures, is formed when a mixture of equal volumes of hydrogen and chlorine is exposed to sunlight, or the light from burning magnesium. Under these conditions the combination takes place with such rapidity as to produce an explosion Hydrochloric acid is also produced when chlorine acts on many organic bodies containing hydrogen. If a piece of filter-paper be moistened with turpentine and placed in a jar of chlorine gas, the turpentine is at once decomposed with the production of hydrochloric acid, and the heat produced is sufficient to ignite the paper. Hydrochloric acid is also produced when a chloride is treated with sulphuric acid. In the case of sodium chloride, if the action takes place at ordinary temperatures, sodium hydrogen sulphate is formed—

$$NaCl+H_2SO_4=NaHSO_4+HCl.$$

But at high temperatures the sodium acid sulphate decomposes another molecule of sodium chloride, more hydrochloric acid being evolved—

$$NaHSO_4+NaCl=Na_2SO_4+HCl.$$

Commercial hydrochloric acid is obtained in this manner as a by-product in the manufacture of sodium carbonate by the Leblanc process (*q.v.*), the gas produced being dissolved in water. The solution contains from 30 to 32 per cent of hydrochloric acid, and has a specific gravity of about 1·16. The maximum quantity which water will dissolve corresponds to a specific gravity of 1·21 or 43 per cent. of real hydrochloric acid At 0° C. 1 volume of water dissolves 525 volumes of hydrochloric acid gas. Commercial hydrochloric acid, also termed spirits of salt and muriatic acid, is a yellow liquid, its colour being due to the presence of impurities The chief of these are sodium sulphate and chloride, iron, arsenic, oxides of nitrogen, and free chlorine The Castner-Kellner Co. have recently introduced a very pure form of hydrochloric acid, termed synthetic, made by the direct union of hydrogen and chlorine When a saturated aqueous solution of hydrochloric acid is exposed to air, some of the gas is given off This becoming partly condensed, gives rise to what are known as fumes. The aqueous solution has a strongly acid reaction to litmus, and an acid taste When a dilute aqueous solution of hydrochloric acid is boiled, it at first loses only water until the concentration of the acid rises to 20·24 per cent When this point is reached, the liquid distils over unchanged at a constant boiling-point of 110° C at atmospheric pressure Conversely, when a concentrated solution is boiled, hydrochloric acid gas is first given off till the mixture contains 20·24 per cent of acid The strength of the acid at this constant boiling-point corresponds to the formula $HCl\,8H_2O$. Hydrochloric acid is monobasic It neutralises bases, oxides, or hydroxides, forming salts termed chlorides—

$$CaO+2HCl=CaCl_2+H_2O,$$
$$Ca(OH)_2+2HCl=CaCl_2+2H_2O.$$

The chlorides are, with few exceptions, readily soluble in water Among the more important are sodium chloride, $NaCl$, calcium chloride, $CaCl_2$, barium chloride, $BaCl_2$, magnesium chloride, $MgCl_2$, aluminium chloride, Al_2Cl_6; and zinc chloride, $ZnCl_2$ These compounds will be referred to again in Chapter XXIX

The Analysis of Hydrochloric Acid.—The approximate strength of a sample of commercial hydrochloric acid may be ascertained by taking its specific gravity at 15° C by means of a hydrometer and referring to table on p 342

For a more exact estimation the titration method should be employed From 10 to 20 c.c of the sample are weighed in a stoppered weighing bottle, washed into a 500 c c flask, and diluted to the mark with distilled water. A convenient volume is then withdrawn with a pipette and titrated with normal sodium hydroxide, using methyl orange as indicator Each cubic centimetre of normal alkali neutralises 0·0365 gramme of hydrochloric acid

For the determination of salts a weighed quantity of the acid is evaporated to dryness on a water-bath in a weighed silica or platinum dish. The residue is ignited gently, cooled, and weighed. It is then dissolved in water, filtered if necessary, and made up to a definite volume Sodium chloride is determined in a portion of the solution by titration with decinormal silver nitrate solution with potassium chromate as indicator (factor 1 c.c. N/10 silver nitrate=0·00585 gramme sodium chloride). A second portion is placed in a beaker, made acid

HYDROCHLORIC ACID

Bé°	Sp gr.	Tw°	%HCl	Bé°	Sp. gr	Tw°	%HCl	Bé.°	Sp gr.	Tw.°	%HCl.
1·00	1·0069	1·38	1·40	16 0	1 1240	24·80	24·57	20 8	1 1675	33 50	32·93
2·00	1·0140	2 80	2 82	16 1	1 1248	24 96	24 73	20 9	1 1684	33 68	33·12
3 00	1 0211	4 22	4 25	16·2	1 1256	25 12	24·90	21 0	1 1691	33 88	33·31
4 00	1 0284	5·68	5·69	16 3	1 1265	25 30	25 06	21 1	1·1703	34 06	33 50
5 00	1 0357	7 14	7·15	16·4	1 1274	25·48	25·23	21 2	1·1713	34 2›	33 69
5·25	1·0375	7·50	7·52	16·5	1·1283	25 66	25·39	21·3	1 1722	34·44	33 88
5 50	1 0394	7·88	7 89	16 6	1 1292	25 84	25 56	21 4	1 1732	34 64	34 07
5 75	1 0413	8·26	8 26	16·7	1 1301	26 02	25·72	21·5	1 1741	34 82	34·26
6 00	1 0432	8·64	8 64	16 8	1 1310	26 20	25 89	21 6	1·1751	35 02	34·45
6 25	1 0450	9 00	9 02	16 9	1 1319	26 38	26 05	21·7	1 1760	35·20	34 64
6 50	1·0469	9 38	9 40	17 0	1·1328	26 56	26 22	21·8	1 1770	35 40	34 83
6·75	1·0488	9 76	9 78	17 1	1 1336	26 72	26 39	21 9	1·1779	35 58	35 02
7 00	1 0507	10 14	10·17	17 2	1·1345	26 90	26 56	22·0	1·1789	35·78	35 21
7·25	1 0526	10 52	10 55	17 3	1·1354	27 08	26 73	22 1	1·1798	35 96	35 40
7·50	1·0545	10 90	10 94	17 4	1 1363	27 26	26 90	22 2	1·1808	36 16	35 59
7 75	1 0564	11 28	11 32	17 5	1 1372	27 44	27 07	22 3	1 1817	36 34	35·78
8 00	1 0584	11 68	11·71	17 6	1 1381	27 62	27 24	22 4	1·1827	36 54	35 97
8 25	1 0603	12 06	12 09	17 7	1 1390	27 80	27·41	22 5	1 1836	36 72	36·16
8 50	1 0623	12 46	12 48	17 8	1 1399	27 98	27 58	22 6	1·1846	36 92	36·35
8 75	1·0642	12 84	12 87	17 9	1 1408	28 16	27 75	22 7	1·1856	37 12	36·54
9 00	1 0662	13 24	13 26	18 0	1 1417	28 34	27 92	22 8	1 1866	37 32	36·73
9 25	1 0681	13 62	13 65	18 1	1 1426	28 52	28 09	22 9	1 1875	37 50	36 93
9 50	1 0701	14 02	14 04	18 2	1 1435	28 70	28·26	23 0	1 1885	37 70	37 14
9 75	1 0721	14 42	14 43	18 3	1 1444	28 88	28 44	23 1	1 1895	37 90	37 36
10 00	1·0741	14 82	14 83	18 4	1 1453	29 06	28 61	23 2	1·1904	38·08	37 58
10 25	1 0761	15 22	15 22	18 5	1 1462	29 24	28 78	23·3	1·1914	38 28	37 80
10 50	1 0781	15 62	15 62	18 6	1 1471	29 42	28 95	23 4	1 1924	38 48	38 03
10 75	1 0801	16 02	16 01	18 7	1 1480	29 60	29 13	23 5	1 1934	38 68	38 26
11 00	1 0821	16 42	16 41	18 8	1 1489	29 78	29 30	23 6	1·1944	38 88	38 49
11 25	1 0841	16 82	16 81	18 9	1 1498	29 96	29 48	23·7	1 1953	39 06	38 72
11 50	1 0861	17 22	17 21	19 0	1 1508	30 16	29 65	23 8	1 1963	39 26	38 95
11 75	1 0881	17·62	17 61	19·1	1 1517	30 34	29 83	23 9	1·1973	39 46	39 18
12 00	1 0902	18 04	18 01	19 2	1 1526	30 52	30 00	24 0	1·1983	39 66	39 41
12 25	1·0922	18·44	18·41	19 3	1 1535	30 70	30 18	24 1	1 1993	39 86	39 64
12 50	1 0943	18 86	18 82	19 4	1 1544	30 88	30 35	24 2	1 2003	40 06	39 86
12 75	1 0964	19 28	19 22	19 5	1·1554	31·08	30 53	24 3	1 2013	40·26	40 09
13 00	1 0985	19 70	19 63	19 6	1 1563	31 26	30 71	24 4	1·2023	40 46	40 32
13 25	1 1006	20 12	20 04	19 7	1 1571	31·44	30 90	24 5	1 2033	40 66	40 55
13 50	1·1027	20 54	20 45	19 8	1 1581	31 62	31·08	24 6	1 2043	40 86	40 78
13 75	1 1048	20 96	20 86	19 9	1 1590	31·80	31·27	24 7	1·2053	41 06	41 01
14 00	1 1069	21 38	21 27	20 0	1 1600	32 00	31 45	24·8	1 2063	41·26	41 24
14 25	1 1090	21 80	21 68	20 1	1 1609	32 18	31 64	24 9	1 2073	41·46	41 48
14 50	1 1111	22 22	22 09	20 2	1 1619	32 38	31 82	25 0	1 2083	41 66	41·72
14 75	1 1132	22 64	22 50	20·3	1 1628	32 56	32 01	25 1	1·2093	41 86	41 99
15 00	1 1154	23 08	22 92	20·4	1 1637	32 74	32 19	25·2	1 2103	42 06	42 30
15 25	1 1176	23 52	23 33	20 5	1 1647	32 94	32 38	25 3	1·2114	42 28	42 64
15 50	1·1197	23 94	23 75	20 6	1 1656	33·12	32 56	25·4	1 2124	42 48	43 01
15 75	1·1219	24·38	24·16	20 7	1·1666	33 32	32 75	25 5	1·2134	42·68	43·40

ALLOWANCE FOR TEMPERATURE

10°–15° Bé. — 1/40° Be or 0 0002 sp gr. for 1° F.
15°–22 Be — 1/50° Bé. or 0·0003 „ „ 1° F.
22°–25° Bé. — 1/28° Bé. or 0·0035 „ „ 1° F.

with hydrochloric acid, and precipitated at the boiling-point with barium chloride solution. Any barium sulphate formed is filtered off, washed, ignited, and weighed. Iron may be estimated colorimetrically by means of potassium ferrocyanide in another portion of the solution Free chlorine is detected in the original sample by diluting a portion and adding a little potassium iodide and starch solution. Nitric acid may be recognised by the brown ring or diphenylamine tests.

Occasionally free sulphuric acid is present. This is rather difficult to estimate in the presence of hydrochloric acid and sodium sulphate. The following method is suitable :—

1. First, determine the total acidity by titration.
2 Then estimate the total sulphates by precipitation with barium chloride solution.
3 Finally, determine sodium sulphate in the residue after evaporation and ignition.

The difference between the total SO_3 and that in the residue is converted into free sulphuric acid. The equivalent of this in normal sodium hydroxide is then deducted from the total acidity obtained by titration, the difference being acidity due to hydrochloric acid alone.

Nitric Acid, HNO_3, or *aqua fortis*, is made by heating a mixture of sodium nitrate and sulphuric acid to about 100° C in cast-iron retorts and condensing the vapour which distils over The reaction takes place in two stages, acid sodium sulphate being produced at low temperatures—

$$NaNO_3+H_2SO_4=NaHSO_4+HNO_3,$$
$$2NaNO_3+H_2SO_4=Na_2SO_4+2HNO_3$$

The nitric acid distils over and condenses to a brownish liquid This brown colour is due to the presence of oxides of nitrogen, which are produced by the action of heat on nitric acid—

$$4HNO_3=4NO_2+2H_2O+O_2.$$
nitrogen peroxide

Nitric acid containing dissolved oxides of nitrogen is termed "fuming" nitric acid The commercial acid is purified by mixing it with concentrated sulphuric acid and redistilling The oxides of nitrogen are driven out by heating the acid and blowing air through it. Pure nitric acid is a colourless liquid which has a specific gravity of 1·56 at 0° C It is hygroscopic, and fumes when brought into contact with moist air. It is soluble in water in all proportions When it is mixed with cold water, heat is evolved and subsequent contraction takes place, as in the case of sulphuric acid. The greatest contraction occurs when nitric acid and water are present in the proportions of HNO_3 $3H_2O$. Pure nitric acid boils at 86° C. at atmospheric pressure, but an aqueous solution behaves in the same manner as one of hydrochloric acid when heated Concentrated solutions lose acid and dilute solutions water till a solution containing 68 per cent. of acid is produced which distils unchanged at 120·5° C., and has a specific gravity of 1·414.

Nitric acid is both an acid and a powerful oxidising agent. It owes its oxidising properties to the readiness with which it is decomposed into oxides of nitrogen and oxygen. Nitric acid is a compound of nitrogen pentoxide, N_2O_5, with water—

$$N_2O_5+H_2O=2HNO_3.$$

Nitrogen pentoxide, or nitric anhydride, can be made by mixing nitric acid with phosphorus pentoxide, P_2O_5, in a retort and heating the mixture gently. Phosphorus pentoxide is a very powerful dehydrating agent. It takes water from the nitric acid forming metaphosphoric acid, HPO_3—

$$2HNO_3+P_2O_5=N_2O_5+2HPO_3.$$

When the retort is heated to about 47° C. the nitrogen pentoxide passes over and is condensed in ice cooled water. When the distillate is frozen, crystals of nitrogen pentoxide are produced. Nitrogen pentoxide is an unstable body, breaking down readily into oxygen and nitrogen peroxide, NO_2—

$$2N_2O_5=4NO_2+O_2.$$

This nitrogen peroxide can also give up oxygen under suitable conditions, becoming changed into a gaseous oxide termed nitric oxide, NO—

$$2NO_2=2NO+O_2.$$

Hence, when nitric acid acts as an oxidising agent, nitric oxide, NO, is generally produced Thus

$$S+2HNO_3=H_2SO_4+2NO$$
$$2FeS_2+10HNO_3=Fe_2(SO_4)_3+H_2SO_4+10NO+4H_2O.$$

But when nitric oxide comes into contact with air it combines with oxygen, forming red fumes of nitrogen peroxide—

$$NO+O=NO_2$$

Nitric acid is used in the laboratory both for destroying organic matter and as an oxidising agent

Its oxidising action on cellulose has been described already When nitric acid is mixed with hydrochloric acid, free or nascent chlorine and nitrosyl-chloride are produced—

$$HNO_3+3HCl=2H_2O+NOCl+Cl_2.$$

This mixture is known as *aqua regia*, and is the most powerful solvent known for metals, attacking even gold and platinum, forming soluble chlorides. When nitric acid is treated with nascent hydrogen it is reduced to nitrous acid, HNO_2, and finally to ammonia Thus, when some dilute sulphuric acid and reduced iron are added to a cold dilute solution of nitric acid, ammonium sulphate is produced—

$$2HNO_3+8H_2=2NH_3+6H_2O,$$
$$2NH_3+H_2SO_4=(NH_4)_2SO_4.$$

This reaction is made use of in the estimation of nitrates or nitric acid

Nitric acid is monobasic Its salts, the nitrates, are characterised by their invariable solubility in water. They are formed by treating nitric acid with basic metallic oxides, hydroxide, or carbonates Most of the metals are attacked or dissolved by nitric acid, but owing to its oxidising properties, secondary reactions often take place and no hydrogen is evolved Dilute nitric acid dissolves tin, forming a nitrate, $Sn(NO_3)_2$, but when strong acid is used, tin oxide, SnO_2, is formed, when nitric acid acts on metallic mercury, either mercurous nitrate, $Hg(NO_3)_2$, or $Hg_2(NO_3)_2$, is formed, according to whether excess of mercury or nitric acid be present. In all of these cases the hydrogen, instead of being liberated, reduces some of the nitric acid to nitrogen peroxide or a lower oxide of nitrogen.

By selecting suitable metals and using moderately dilute acid all of the oxides of nitrogen may be prepared. Thus.

$4HNO_3+Sn = SnO_2+2H_2O+4NO_2$, nitrogen peroxide.
$6HNO_3+4Ag=4AgNO_3+3H_2O+N_2O_3$, nitrogen trioxide.
$8HNO_3+3Cu=3Cu(NO_3)_2+4H_2O+2NO$, nitrogen dioxide or nitric oxide.
$10HNO_3+4Zn=4Zn(NO_3)_2+5H_2O+N_2O$, nitrogen monoxide.

Analysis of Nitric Acid.—The following table gives the specific gravities of solutions of nitric acid in water —

TABLE SHOWING THE STRENGTH OF NITRIC ACID OF VARIOUS SPECIFIC GRAVITIES.

The numbers marked * are the results of direct observations; the others are obtained by interpolation.

HNO_3 per cent.	Specific Gravity.		HNO_3 per cent.	Specific Gravity.		HNO_3 per cent	Specific Gravity.	
	At 0°.	At 15°.		At 0°.	At 15°		At 5°.	At 15°.
100 00	1 559	1 530	72 39*	1 455*	1 432*	45 00	1 300	1 284
99 84*	1 559*	1 530*	71 24*	1 450*	1 429*	43 53*	1 291*	1 274*
99 72*	1 558*	1 530*	69 96	1 444	1 423	42 00	1·280	1 264
99 52*	1 557*	1 529*	69 20*	1 441	1 419*	41 00	1 274	1 257
97 89*	1 551*	1 523*	68 00	1 435	1 414	40 00	1 267	1 251
97·00	1 548	1 520	67 00	1 430	1 410	39 00	1 260	1 244
96 00	1 544	1 516	66 00	1 425	1 405	37 95*	1 253*	1 237*
95 27*	1 542*	1 514*	65 07*	1 420*	1 400*	36 00	1 240	1 225
94 00	1 537	1 509	64 00	1 415	1 395	35·00	1 234	1 218
93 01*	1 533*	1 506*	63 59	1 413	1 393	33·86*	1 226*	1 211*
92 00	1 529	1 503	62 00	1 404	1 386	32 00	1 214	1 198
91 00	1 526	1 499	61 21*	1 400*	1 381*	31 00	1 207	1 192
90 00	1 522	1 495	60 00	1 393	1 374	30 00	1 200	1 185
89 56*	1 521*	1 494*	59·59*	1 391*	1·372*	29·00	1·194	1 179
88·00	1 514	1 488	58 88	1·387	1 368	28 00*	1 187*	1 172*
87·45*	1 513*	1 486*	58 00	1·382	1 363	27 00	1 180	1 166
86 17*	1 507*	1 482*	57 00	1 376	1 358	25 71*	1 171*	1 157*
85 00	1 503	1 478	56 10*	1 371*	1 353*	23 00	1·153	1 138
84 00	1 499	1 474	55 00	1 365	1 346	20 00	1 132	1 120
83 00	1·495	1 470	54 00	1 359	1 341	17 47*	1 115*	1·105*
82 00	1·492	1 467	53 81	1 358	1 339	15 00	1 099	1 089
80 96*	1·488*	1 463*	53 00	1 353	1 335	13 00	1 085	1 077
80 00	1 484	1 460	52 33*	1 349*	1·331*	11 41*	1·075	1 067*
79 00	1·481	1 456	50 99*	1 341*	1·323*	7 22*	1 050	1 045*
77 66	1 476	1 451	49 97	1 334	1 317	4 00	1 026	1·022
76 00	1·469	1·445	49 00	1·328	1 312	2 00	1 013	1 010
75 00	1 465	1·442	48 00	1 321	1 304	0 00	1 000	0 999
74·01*	1·462*	1·438*	47 18*	1·315*	1·298*			
73·00	1·457	1·435	46 64	1·312	1 295			

Nitric acid is estimated by titration in the manner described for hydrochloric acid (1 c.c N/1 alkali=0·063 gramme of nitric acid).

Sulphuric acid and salts can also be tested for in the same way.

Acetic acid, CH_3COOH, may be made by oxidising either aldehyde or alcohol by means of air in the presence of platinum black, or by an acid solution of potassium permanganate—

$$CH_3CHO+O=CH_3COOH,$$
$$CH_3.CH_2OH+O_2=CH_3COOH+H_2O.$$

Alcohol is also converted into acetic acid by a process of fermentation brought about by *Mycoderma aceti*, and this is made use of in the manufacture of vinegar. A dilute extract of malt in water is fermented, by means of yeast, till the sugar it contains is changed into alcohol The alcohol solution is then allowed to trickle over wooden chips of twigs upon which *Mycoderma aceti* (or mother of vinegar) is growing, air at the same time being supplied Only dilute solutions of acetic acid can be obtained in this way, since the ferment will not act in concentrated solution of either alcohol or acetic acid Vinegar contains from 4 to 6 per cent of acetic acid

Commercial acetic acid is made, commonly, from " pyroligneous " acid, which is obtained when wood is distilled in a closed retort A mixture of bodies, including methyl alcohol, CH_3OH, acetone, CH_3COCH_3, acetic acid, and tar is obtained, while charcoal remains in the retort If the vapours are passed through hot milk of lime the acetic acid forms calcium acetate, while the volatile alcohol and acetone pass on and are afterwards condensed The calcium acetate thus obtained is distilled with hydrochloric acid and the acetic acid condensed—

$$(CH_3COO)_2Ca + 2HCl = 2CH_3COOH + CaCl_2$$

Pure acetic acid is prepared from this commercial product by neutralising it with potassium carbonate and crystallising the potassium acetate This is then heated till it is anhydrous and distilled with pure sulphuric acid Acetic acid is a colourless liquid which crystallises at 16 7° C and boils at 118° C Its specific gravity at 0° C is 1 080 The crystalline acid is known as ' glacial " acetic acid The addition of a little water lowers the melting point of the crystals considerably Acetic acid dissolves in water in all proportions When water is added to glacial acetic acid heat is evolved, and on cooling the mixture its volume contracts The greatest contraction corresponds to the formula $(CH_3COOH)H_2O$ Acetic acid is soluble also in alcohol or ether It is itself a good solvent for many organic compounds such as cellulose acetates, and also some inorganic bodies such as iodine

Acetic acid is not so " strong " an acid as the common mineral acids Thus, it does not decompose sodium sulphate But it liberates carbonic acid from carbonates—

$$CaCO_3 + 2CH_3COOH = (CH_3COO)_2Ca + CO_2 + H_2O$$

It does not tender cotton like the strong acids, but in very dilute solutions produces a ' scroop ' It dissolves many metals forming acetates and liberating hydrogen A mixture of iron and acetic acid is used as a reducing agent—

$$Fe + 2CH_3COOH \quad Fe(CH_3COO)_2 + H_2$$

Acetic acid is monobasic The acetates are generally soluble crystalline compounds which are readily decomposed by stronger acids with the liberation of acetic acid

$$CH_3COONa + HCl = NaCl + CH_3COOH$$

Acetic acid may be identified by changing it into ethyl acetate, which has a characteristic smell Moreover, when a solution of acetic acid is boiled, the acid is expelled and has itself the characteristic smell of vinegar If acetic acid be mixed with a little alcohol and sulphuric acid and the mixture warmed gently, ethyl acetate is produced—

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O$$

To detect acetic acid in a dilute solution it should be neutralised with sodium

hydroxide and evaporated to dryness. The residue is then placed in a test-tube with a little alcohol and a slight excess of strong sulphuric acid, and warmed gently

When a solution of acetic acid is exactly neutralised with sodium hydroxide and a neutralised solution of ferric chloride is added, a red colour, due to ferric acetate, is produced. If the mixture be boiled, a more basic salt is precipitated and acetic acid is liberated. At the same time, unless excess of ferric chloride is present, the solution becomes colourless The reactions are—

$$FeCl_3+3CH_3COONa=3NaCl+(CH_3COO)_3Fe,$$
$$(CH_3COO)_3Fe+H_2O=(CH_3COO)_2(OH)Fe+CH_3COOH.$$

Estimation of Acetic Acid.—Acetic acid containing water corresponding to the formula $C_2H_4O_2\,H_2O$ has a greater specific gravity than the anhydrous acid Owing to this fact the strength of a concentrated solution of acetic acid cannot be determined from the density, although the method may be used for dilute solutions The following table, due to Oudemanns and Mohr, is given by Allen (*Commercial Organic Analysis*, vol. 1):—

Specific Gravities of Solutions of Acetic Acid.

$C_2H_4O_2$ per cent	Specific Gravity		$C_2H_4O_2$ per cent	Specific Gravity.	
	Oudemanns	Mohr.		Oudemanns.	Mohr
1	1 0007	1 001	21	1 0298	1 029
2	1 0022	1 002	22	1 0310	1 031
3	1 0037	1 004	23	1 0324	1 032
4	1 0052	1 005	24	1 0337	1 033
5	1 0067	1 007	25	1 0350	1 034
6	1 0083	1 008	26	1 0363	1 035
7	1 0098	1 010	27	1 0375	1 036
8	1 0113	1 012	28	1 0388	1 038
9	1 0127	1 013	29	1 0400	1 039
10	1 0142	1 015	30	1 0412	1 040
11	1 0157	1 016	31	1 0424	1 041
12	1 0171	1 017	32	1 0436	1 042
13	1 0185	1 018	33	1 0447	1 044
14	1 0200	1 020	40	1 0523	1 051
15	1 0214	1 022	50	1 0615	1 061
16	1 0228	1 023	60	1 0685	1 067
17	1 0242	1 024	70	1 0733	1 070
18	1 0256	1 025	77	1 0748	1 0735
19	1 0270	1 026	80	1 0748	1 0735
20	1·0284	1 027	90	1 0713	1 0730
			100	1 0553	1 0635

It will be seen from this table that the specific gravities of 100 per cent. and 43 per cent. are the same. The strength of a sample of acetic acid is determined by titration But acetic acid is not sensitive to methyl orange. Either phenolphthalein or litmus must be used as the indicator. Each cubic centimetre of normal sodium hydroxide neutralises 0·06 gramme of acetic acid.

Commercial acetic acid may contain the following impurities: Sulphuric acid and sulphates, sulphurous acid, hydrochloric acid and chlorides, copper and lead. Sulphuric acid or sulphates are indicated by the formation of a

precipitate with barium chloride solution They are estimated in the manner described for hydrochloric acid Hydrochloric acid and chlorides form a precipitate with silver nitrate solution If a weighed quantity of the acid be diluted with water, slightly acidified with nitric acid, and boiled with excess of silver nitrate solution, the total chlorides present are precipitated as insoluble silver chloride This precipitate is filtered off on a silica gooch crucible, well washed, ignited very gently, and weighed The weight of silver chloride obtained multiplied by 0 2479 gives the total chlorine present as chlorides and hydrochloric acid If, then, some of the acid be evaporated to dryness, the chlorine present as chloride can be titrated in the residue by means of decinormal silver nitrate solution and potassium chromate

Sulphurous acid can be detected and estimated by distilling some of the acid with steam into bromine water This oxidises sulphurous to sulphuric acid A little hydrochloric acid is added to the distillate, which is then boiled till the excess of bromine is expelled Barium chloride solution is then added and the boiling continued The precipitated barium sulphate is filtered off, weighed, and converted into sulphur dioxide, SO_2, by multiplying by 0 274

Calcium salts, which are occasionally present, may be precipitated as calcium oxalate by neutralising with ammonia and boiling with ammonium oxalate Copper and iron are indicated by their reactions with a solution of potassium ferrocyanide This gives a reddish brown colour or precipitate in the presence of copper If much iron be also present, this reaction may be masked by the blue colour due to the iron In this case the copper should be precipitated as sulphide by means of sulphuretted hydrogen, the precipitate filtered off and identified by dissolving in nitric acid, evaporating to dryness and applying the potassium ferrocyanide test to the residue

Tartaric acid (dihydroxy succinic acid), $CH(OH)COOH\,CH(OH)COOH$, is used sometimes instead of acetic acid for producing scroop on bleached or mercerised cotton It occurs in many fruits, notably in ripe grapes When grape juice is fermented in the manufacture of wine, potassium hydrogen tartrate (or argol) is deposited Both tartaric acid and normal potassium tartrate are prepared from argol After purification by dissolving in hot water and crystallising, it is boiled with calcium carbonate or chalk A precipitate of insoluble calcium tartrate is produced, and normal potassium tartrate remains in the solution—

$$2C_4H_5O_6K+CaCO_3=C_4H_4O_6Ca+C_4H_4O_6K_2+CO_2+H_2O$$

If the solution be treated with calcium chloride, more calcium tartrate is formed together with potassium chloride—

$$C_4H_4O_6K_2+CaCl_2=C_4H_4O_6Ca+2KCl$$

When calcium tartrate obtained by these reactions is treated with the necessary quantity of dilute sulphuric acid, tartaric acid is liberated, and since it is soluble, it can be removed by filtration from the sparingly soluble calcium sulphate and purified by crystallisation—

$$C_6H_4O_6Ca+H_2SO_4=C_6H_6O_6+CaSO_4$$

Tartaric acid is a colourless crystalline soluble substance melting at 167° C, but becoming at the same time charred It dissolves also in alcohol, but is insoluble in ether When treated with concentrated sulphuric acid it dissolves and becomes charred The reaction takes place very rapidly if the mixture be heated, a black mass of carbon being produced Tartaric acid is dibasic, forming

both acid and normal salts. Potassium hydrogen tartrate (argol or cream of tartar) is used in dyeing. It is only sparingly soluble in cold water. Rochelle salt or potassium sodium tartrate, $C_4H_4O_6KNa\ 4H_2O$, is used in making Fehling solution. Potassium antimony tartrate (tartar emetic) is of importance also, since it is used for fixing tannic acid in the mordanting cotton. Its formula is $C_4H_4O_6K(SbO)\frac{1}{2}H_2O$.

Oxalic acid, $C_2H_2O_4$, or COOH, is a colourless crystalline substance which

COOH

crystallises with two molecules of water, $C_2H_2O_4\ 2H_2O$. It is made by heating sawdust with caustic potash, potassium oxalate being formed as one product. The fused mass is extracted with water and filtered. The filtrate is then heated with lime, when insoluble calcium oxalate is produced—

$$C_2O_4K_2+Ca(OH)_2=2KOH+CaC_2O_4$$

The calcium oxalate is collected and decomposed with dilute sulphuric acid. After concentration, the calcium sulphate is filtered off and the oxalic acid allowed to crystallise.

Oxalic acid is fairly soluble in water; at 10° C 100 parts of water dissolve 8 of the acid. The aqueous solution has a strongly acid reaction. Oxalic acid is dibasic, giving two potassium salts, COOH COOK and $(COOK)_2$.

When heated with strong sulphuric acid, it is decomposed into a mixture of carbon dioxide and carbon monoxide—

$$C_2O_4H_2-H_2O=CO_2+CO.$$

When treated with potassium permanganate in the presence of sulphuric acid, it yields carbon dioxide—

$$5C_2O_4H_2+2KMnO_4+3H_2SO_4=10CO_2+8H_2O+K_2SO_4+2MnSO_4.$$

With the exception of the salt of the alkali metals and ammonium, the oxalates are generally insoluble in water But the iron salts are comparatively soluble Salts of lemon, or acid potassium oxalate, $C_2O_4HK\ C_2O_4H_2\ 2H_2O$, is used to remove iron stains from fabrics Calcium oxalate, C_2O_4Ca, is of importance in the estimation of calcium.

Lime (Calcium Oxide), CaO.—Lime is made by igniting (known as "burning") chalk or limestone in a kiln—

$$CaCO_3 \rightleftharpoons CaO+CO_2.$$

The reaction is reversible, calcium carbonate being re-formed when lime is brought into contact with carbon dioxide at ordinary temperatures. When made from chalk, comparatively pure calcium oxide is obtained, but many limestones contain magnesium carbonate and, sometimes, compounds of iron and aluminium, in the form of clay When clay limestones are burnt, "hydraulic" lime or cement is produced which is capable of setting under water.

Commercial calcium oxide, or quicklime, is a white substance generally in the form of lumps. It combines readily with water, forming calcium hydroxide, or slaked lime, the reaction being accompanied by the evolution of much heat.

Calcium hydroxide has a strongly alkaline reaction, caustic properties, and is a typical base

When a small quantity of water is poured upon lime the combination with water is accompanied by the evolution of heat, causing part of the water to be converted into steam The slaking of lime is more rapid at high than at low

temperatures, even magnesia slaking in about six hours at 100° C. At ordinary temperatures, forty-eight hours is often necessary, while magnesia requires some weeks For the rapid slaking of lime it is important to use neither too much nor too little water If too little is used, the lime will only be partly slaked, and this will cake and protect the remainder from the action of the water On the other hand, too great an excess of water lowers the temperature This hinders the slaking, and the mass does not readily powder as it slakes The best plan is to put the lime in a shallow vessel with just enough water to thoroughly wet it, and after twenty-four hours add sufficient to convert it into a stiff paste (Procter, *Principles of Leather Manufacture*, p 123) In the form of a paste it keeps well and may be dug out as required When stored dry, it rapidly absorbs carbon dioxide from the air and becomes useless

Lime is only slightly soluble in water, a saturated solution containing approximately 1 gramme per litre The solubility diminishes with rise of temperature. In the presence of magnesia, stronger solutions are obtained than from pure lime, the magnesia being soluble in a saturated solution of calcium hydroxide The following table (Guthrie, *J S C I*, 1901, p 224) shows the effect of temperature on the solubility of lime in water —

100 c c	of saturated	lime water at	5° C	contain 0 1350 grm	of CaO
,,	,,	10°	,,	0 1342	,,
,,	,,	15°	,,	0 1320	,,
,,	,,	20°	,,	0 1293	,,
,,	,,	25	,,	0 1254	,,
,,	,,	30°	,,	0 1219	,,
,,	,,	35°	,,	0 1161	,,
,,	,,	40°	,,	0 1119	,,
,,	,,	50°	,,	0 0981	,,
,,	,,	60°	,,	0 0879	,,
,,	,,	70°	,,	0 0781	,,
,,	,,	80	,,	0 0740	,,
,,	,,	90	,,	0 0696	,,
,,	,,	100	,,	0 0597	,,

A saturated solution of lime in water at 15° C is approximately a N/20 solution A solution of cane sugar in water dissolves lime much more readily than water alone, forming calcium saccharosate, $C_{12}H_{20}(CaOH)_2O_{11}$ The solution, like that in water, has strongly marked alkaline properties, and is decomposed by carbon dioxide, sucrose and calcium carbonate being formed

Calcium hydroxide has the power of saponifying fats, but insoluble calcium soaps are produced With triolein the reaction is expressed by the equation

$$2(C_{17}H_{33}COO)_3C_3H_5+3Ca(OH)_2=2C_3H_5(OH)_3+3(C_{17}H_{33}COO)_2Ca$$

Lime is used in two forms, viz (1) milk of lime, and (2) lime water

Milk of lime consists of very finely ground lime suspended in water The lime, having been ground, is mixed with water in a mechanical mixer till it has the consistency of thin cream Great care must be taken to ensure that no unslaked lumps or small particles are left When using milk of lime, the quantity required for each operation should be weighed out and the whole of it used. Milk of lime is very difficult to measure, owing to the rapidity with which it settles This forms the chief objection to its use Another is that one is using a solid reagent of only limited solubility, and, hence, its complete action can only be ensured by very thorough mixing with the water

Lime Water —The difficulties connected with the use of milk of lime can be overcome to a certain extent by substituting saturated lime water, which has

also a distinct advantage, namely, that the reagent is introduced in solution, instead of being merely suspended in water as is the case with milk of lime. The disadvantages attending the use of lime water are, first, the large volume which is necessary, owing to the limited solubility of calcium oxide in water; and, secondly, the difficulty of obtaining a solution of constant concentration. When lime water is used in water softening, it is generally made in an automatic saturator, through which a continuous stream of water flows, governed by an automatic valve connected with the precipitation chamber.

Commercial lime varies in composition, according to the nature of the limestone from which it is made. A good sample should contain at least 95 per cent. of calcium oxide. Lime made from a limestone which contains magnesium carbonate will be contaminated with magnesium oxide This is of no use either for water softening or for lye boiling.

When magnesia is present in lime used for lye boiling it may cause tendering, owing to the slowness with which it combines with water. If lime has been underburnt a considerable proportion of 'unchanged' calcium carbonate may remain, while if overburnt some of the lime may be converted into calcium silicate.

The following percentage analyses of good and bad limes illustrate the variations met with :—

	1.	2.	3	4.
Silica and insoluble matter . .	0 51	17 70	1 88	
Iron oxide and aluminium oxide .	0 17	6 42	4 00	
Calcium oxide	97 29	49 86	55 97	91 95
,, carbonate	1 05	14 21	1 50	
,, sulphate . . .	1 96	3 01	0 51	
,, chloride . . .	..	0 33		
Magnesium oxide .	0 05	2 09	30 44	1 30

The Analysis of Lime.—The most important determination is the percentage of calcium oxide, generally termed " available lime " For this, 1 gramme of the sample, very finely powdered, is washed into a litre flask with a little carbon dioxide free distilled water. Sufficient boiling distilled water is then added to bring the volume to 1000 c.c. The stopper is replaced and the contents of the flask mixed frequently during the next six hours The volume is then adjusted to the mark with cold carbon dioxide free water and, after mixing again, allowed to settle Fifty c.c. of the clear solution are withdrawn and titrated with decinormal acid, using phenolphthalein as indicator Each cubic centimetre used corresponds to 0·0028 gramme of calcium oxide If a solution of cane sugar be used a greater weight than 1 gramme may be taken. The following process is recommended by Heidrick (*Analyst*, 1907, p. 324) In a 500 c.c. flask are placed 10 c c. of alcohol, and 5 grammes of the finely powdered lime are added. The flask is filled to the mark with a 10 per cent solution of cane sugar, and at once placed on a shaker and shaken for at least four hours. A portion is then filtered rapidly and titrated with decinormal hydrochloric acid, using methyl orange as indicator It may be noted that a solution of cane sugar does not dissolve magnesium oxide.

Carbon dioxide may be determined gravimetrically by means of Schrotter's apparatus. This is essentially a flask with three openings—that at A (fig 126)

closed by a glass stopper, is for the introduction of a weighed quantity of the substance; at B, a tap-funnel (also closed with a stopper) admits dilute sulphuric acid; C is a tube which allows the liberated CO_2 to escape after thorough drying by the strong sulphuric acid it contains. From 2 to 3 grammes of the lime are weighed into the flask of the apparatus, the tap-funnel is nearly filled with dilute sulphuric acid, and the drying tube half filled with strong sulphuric acid. The stoppers, slightly greased, are inserted and the apparatus weighed. Acid from the funnel is then very slowly admitted to the flask, so that the carbon dioxide escapes in single bubbles, passing through the strong sulphuric acid in the drying tube at a rate not faster than two per second. When effervescence has ceased the remaining dilute acid is run in, the tap opened, and the flask gradually heated until boiling just begins. At the same time the gaseous contents of the flask are aspirated by connecting the tube at the top of the drying apparatus with an aspirator or simply sucking carefully with the mouth Aspiration must not be unduly prolonged. When at an end, the stopper is replaced in the tap-funnel, the apparatus allowed to cool and then weighed To prevent the strong sulphuric acid in the drying tube from absorbing moisture from the air, it should be closed during weighing by a bit of rubber tubing plugged with a glass rod. The loss of weight of the apparatus is the amount of carbon dioxide in the weight of lime taken.

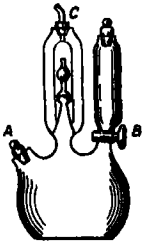


FIG 126 — Schrotter's apparatus

When the percentage of available lime is satisfactory a more detailed analysis is rarely necessary. But sometimes the estimation of the remaining constituents is required. This may be carried out as follows .—

1 **Matter Insoluble in Hydrochloric Acid (chiefly Silica).**—About 5 grammes of the finely powdered sample are weighed into a porcelain dish, and about 25 c.c of hydrochloric acid diluted with distilled water are added. The dish is covered with an inverted funnel, and after effervescence has ceased its contents boiled gently on a sand-bath for about fifteen minutes The funnel is then washed with distilled water, the washings being collected in the dish, the contents of which are evaporated to dryness on the water-bath, and finally baked in an air-oven to render the silica insoluble The residue is extracted with dilute hydrochloric acid and filtered into a 250 c c flask, the filter being washed with distilled water till free from acid. The filter-paper containing the insoluble residue is burnt in a silica or platinum crucible and weighed

2. **Determination of Iron Oxide, Alumina.**—The filtrate is cooled and made up to 250 c c with distilled water Of this, 25 c c., *i e* 0·5 gramme of the sample, are withdrawn with a pipette, placed in a beaker, diluted with water, and made alkaline with ammonia. After boiling gently for a few minutes, the insoluble hydroxides of aluminium and iron are filtered off, washed, dried, ignited, and weighed If it is necessary to determine iron oxide and alumina separately, a second 25 c c. is precipitated in the same way. The washed precipitate is transferred to a beaker, a little sodium peroxide (free from iron) is added, and the contents of the beaker boiled gently This converts the alumina into sodium aluminate, which is soluble in water, but leaves the ferric hydroxide unchanged The latter is filtered off, washed, ignited, and weighed. The alumina is then obtained by difference.

3 **Determination of Calcium.**—The filtrate obtained above is heated until it boils, and 2 grammes of finely powdered ammonium oxalate are then slowly added, with constant stirring, the flame being removed meanwhile. The glass

rod used for stirring is now rinsed into the beaker with distilled water, the contents of the beaker boiled for about two minutes, which causes the precipitate to become dense and more easy to filter. After standing for about half an hour, the supernatant liquid is filtered through a hard filter-paper, the precipitate before transferring to the filter being washed as completely as possible by decantation. The precipitate is dried, ignited, and weighed either as carbonate or lime, as already described for water.

Magnesium.—The filtrate from the lime precipitate is transferred to a conical flask fitted with a well-fitting rubber bung. Sodium phosphate is now added (Na_2HPO_4) and excess of ammonia, the contents of the flask thoroughly shaken for about twenty minutes and then allowed to stand overnight. The resulting precipitate of ammonium-magnesium phosphate is filtered off and washed with a mixture of 1 part of strong ammonia to 3 of water. The washed precipitate is dried, ignited, and weighed as pyrophosphate, the allowance being made as usual, for the solubility of the precipitate in ammonia.

Sulphates.—These are determined in 50 c.c. of the original solution in the same manner as in water.

Chlorides may be detected in the aqueous solution used in the determination of available lime by acidifying with nitric acid and adding silver nitrate solution. If present, they are estimated by dissolving a weighed quantity of the lime in dilute nitric acid, filtering, and precipitating with silver nitrate solution at the *boiling-point*. The precipitate may be collected on a weighed silica Gooch crucible, dried, gently ignited, and weighed.

Barium hydroxide, $Ba(OH)_2$, is used, sometimes, to replace lime and sodium carbonate in water softening. It is made by heating witherite (which is naturally occurring barium carbonate) and slaking the residual barium oxide. It may be made, also, directly by heating the carbonate with superheated steam. Barium hydroxide is a white solid substance which is more soluble in water than calcium hydroxide, 100 parts of water at 100° C. dissolving 101·4 of the hydroxide. The aqueous solution has an alkaline reaction and, when saturated, deposits gradually crystals with the composition $Ba(OH)_2 8H_2O$. When heated, barium hydroxide becomes dehydrated, forming barium oxide, BaO. Barium hydroxide, as a reagent for softening water, has certain advantages over sodium hydroxide and sodium carbonate. Except in the case of magnesium chloride, it removes all kinds of hardness without leaving any soluble salt in solution. In this case, however, the barium chloride which is formed is very stable and unobjectionable. With sulphates of calcium and magnesium insoluble barium sulphate is precipitated, while the calcium hydroxide simultaneously formed is available for the removal of the temporary hardness. The reactions with temporary and permanent hardness are—

$$Ca(HCO_3)_2 + Ba(OH)_2 = CaCO_3 + BaCO_3 + 2H_2O,$$
$$CaSO_4 + Ba(OH)_2 = BaSO_4 + Ca(OH)_2,$$
$$MgCl_2 + Ba(OH)_2 = BaCl_2 + Mg(OH)_2.$$

In many cases the calcium hydroxide produced by the decomposition of calcium sulphate is sufficient to remove all the temporary hardness. Thus, it is often only necessary to consider the permanent hardness. When little calcium sulphate is present, sufficient barium hydroxide must be used to precipitate the temporary hardness remaining after the calcium hydroxide has been used up. The reagent is used in a solution of about 4 per cent. concentration. This solution must be made with soft water which has been boiled to expel carbon dioxide. It is standardised by titration with sulphuric acid.

Strontium hydroxide, $Sr(OH)_2$, has been suggested as a substitute for sodium or calcium hydroxide in lye boiling It is made by heating strontium carbonate with superheated steam Its properties are very similar to those of the corresponding hydroxides of calcium and barium It is a white solid substance which crystallises with 8 molecules of water Its solutions, when treated with hydrogen peroxide, yield crystalline strontium peroxide, $SrO_2\ 8H_2O$ The solubility of strontium hydroxide in water is intermediate between those of calcium and barium hydroxide It saponifies fats with greater facility than calcium hydroxide

Sodium hydroxide, or caustic soda, NaOH, is made by treating a solution of sodium carbonate in water with milk of lime—

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$

The precipitated calcium carbonate is allowed to settle, and the solution of sodium hydroxide is drawn off and concentrated till it sets to a solid mass when cooled It is cast into sticks or lumps, or ground to a powder Concentrated solutions of sodium hydroxide cannot be obtained by this method, because the reaction is reversible, and, when a certain concentration is reached, the sodium hydroxide decomposes the calcium carbonate as quickly as it is formed

Sodium hydroxide is prepared, also, by electrolysing a solution of sodium chloride When an electric current is passed through a solution of sodium chloride, chlorine is liberated at the positive and sodium at the negative, electrode The sodium reacts with water, forming sodium hydroxide and hydrogen, the latter escaping at the negative electrode Thus, a solution of sodium hydroxide collects round the electrode If the positive and negative electrodes are separated by a porous diaphragm, the chlorine gas and solution of sodium hydroxide may be collected separately The chlorine is used for the preparation of liquid chlorine or bleaching powder Commercial sodium hydroxide is not a pure substance It may be purified by dissolving it in alcohol, filtering the solution from the insoluble impurities, and evaporating the filtrate Sodium hydroxide is a white, hard, solid substance, which is the hydroxide of the oxide Na_2O—

$$Na_2O + H_2O = 2NaOH$$

When heated to a dull redness it melts, forming a hard, solid mass when again cooled It is extremely deliquescent, attracting moisture from the air, forming a liquid mass Like all deliquescent bodies, it is very soluble in water, 1 part of hydroxide requiring only 0 47 parts When it dissolves, much heat is generated, the maximum corresponding to the proportions of hydroxide and water represented by the formula $NaOH\ 20H_2O$ When caustic soda is dissolved in water it should be stirred in gradually, or a hard mass is formed which is difficult to deal with When large quantities have to be dissolved the substance is put, sometimes, into a perforated iron chamber which is suspended in a bath of water A scum, consisting of insoluble impurities, generally floats on the surface of a concentrated solution, while other impurities may form a sediment at the bottom of the vessel When sodium hydroxide is exposed to air, it absorbs not only water, but carbon dioxide also, sodium carbonate or bicarbonate being formed Hence, it should be kept in air tight iron drums It cannot be kept in glass vessels, since it attacks them, forming sodium silicate An aqueous solution of sodium hydroxide is strongly alkaline in reaction and has caustic properties It destroys the cuticle of the skin and dissolves animal tissues, such as wool It is a typical base, neutralising acids with the formation of salts and water, thus

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O.$$

When chlorine is passed into a cold solution of sodium hydroxide, a mixture of sodium chloride and sodium hypochlorite is produced, while if the solution of the sodium hydroxide is heated, sodium chlorate is obtained (Chapter XXV.). Aluminium and zinc are dissolved by a solution of sodium hydroxide with the liberation of hydrogen—

$$2NaOH+Zn=H_2+Na_2O_2Zn.$$

A hot solution of sodium hydroxide also dissolves sulphur, giving a mixture of sodium sulphide and sodium thiosulphate—

$$6NaOH+4S=2Na_2S+Na_2S_2O_3+3H_2O.$$

When it is added to a solution of a metallic salt, a hydroxide of the metal is produced, which is obtained as a precipitate if the hydroxide be insoluble in water or in excess of sodium hydroxide solution. Thus, copper and iron are precipitated—

$$CuSO_4+2NaOH=Cu(OH)_2+Na_2SO_4.$$

Some of the hydroxides, such as those of zinc and aluminium, which have both acid and basic properties, dissolve in excess of the reagent, giving salts of the metallic hydroxide—

$$Al_2(SO_4)_3+6NaOH=Al_2(OH)_6+3Na_2SO_4,$$
$$Al_2(OH)_6+6NaOH=\underset{\text{sodium aluminate}}{2Al(ONa)_3}+6H_2O.$$

Sodium hydroxide saponifies fats with the formation of soaps and glycerol. Thus, with olein—

$$(C_{17}H_{33}COO)_3C_3H_5+3NaOH=3C_{17}H_{33}COONa+C_3H_5(OH)_3.$$

Commercial caustic soda is sold either in solution or as a solid. It is sold, generally, on the percentage of sodium oxide, Na_2O, which it contains. This is stated in two ways, namely, (1) as a percentage, and (2) in degrees, *i e* the percentage of sodium oxide *plus* one

The different grades have usually the following strength in degrees 60, 70, 76 to 77 In the powdered form it may also be obtained containing 98 to 99 per cent. of Na_2O. This method of valuation assumes that the whole of the oxide is present as hydroxide, which is, of course, not necessarily the case, but in good varieties the percentage of carbonate is small. The higher grades, though more expensive, are always worth the extra cost The chief impurities are sodium carbonate, chloride, sulphate, silicate, aluminate, and sometimes iron oxide The following analyses are given by Hurst (*Dictionary of Chemicals and Raw Products*) as representative of commercial caustic soda :—

	60 per cent. Cream	60 per cent White.	70 per cent	74 per cent	77 per cent.
Sodium hydroxide . .	75 0	73 0	84 0	96·0	99 34
Sodium carbonate . .	3 1	1·5	4 2	0·2	0 00
Sodium chloride . . .	6·8	19 0	6·0	1·3	0 21
Sodium sulphate . .	1·5	5·5	5·1	1·5	0 10
Sodium silicate . . .	2 1	0 3	0 3	0·1	0 05
Sodium aluminate . .	0 8	trace	trace	0 8	0 30
Sodium sulphite . . .	1 5	...	...	...	...
Insoluble	0 2	...	...	...	...
Water	9 0	...	...	...	...

The superiority of the best grade is very marked, particularly when one remembers that practically all the impurities have an inhibiting effect on the hydrolysis of fats and on pedesis. Caustic soda should be bought on the results of analysis, and great care must be taken in obtaining samples. They must be taken from the drum immediately it is opened, and should be at once transferred to an air-tight stoppered bottle and examined with as little delay as possible. If the sample is left in such a way as to enable it to attract moisture from the air, the results of the analysis will, of course, be too low. This will also be the case if the drum be sampled some time after opening it.

THE ANALYSIS OF SODIUM HYDROXIDE.

The strength of a solution of caustic soda may be determined, approximately, by taking its specific gravity and referring to the following tables —

PERCENTAGES OF CAUSTIC SODA AND CAUSTIC POTASH IN CAUSTIC LYES.

Specific Gravity.	Na_2O Per cent.	NaOH. Per cent	K_2O. Per cent.	KOH. Per cent.
1·0035	0 23	0 30	0 35	0 45
1 0070	0·47	0 61	0 70	0 90
1 0105	0 70	0 90	1 05	1 30
1 0141	0·93	1·20	1 40	1 70
1·0177	1 26	1 60	1 80	2 15
1 0213	1 55	2 00	2 20	2 60
1 0249	1 83	2 36	2 55	3 05
1 0286	2 10	2 71	2 90	3 50
1 0323	2 35	3 03	3·35	4 00
1 0360	2 60	3 35	3 80	4·50
1·0397	2·85	3 67	4 25	5·05
1·0435	3 10	4 00	4·70	5 60
1 0473	3 35	4 32	5 05	6 00
1 0511	3 60	4 64	5 40	6 40
1 0549	3 85	4·96	5 80	6 80
1 0588	4 10	5 29	6 20	7 40
1 0627	4·32	5 58	6·55	7·80
1 0667	4 55	5 87	6·90	8·20
1 0706	4·82	6·21	7 30	8 70
1 0746	5·08	6 55	7·70	9 20
1 0787	5·37	6 76	8 10	9 65
1·0827	5 67	7 31	8 50	10 10
1 0868	5 84	7 66	8 85	10 50
1 0909	6 20	8 00	9 20	10 90
1 0951	6 46	8 34	9 65	11 45
1 1000	6·73	8·68	10 10	12 00
1 1035	7·06	9 05	10 45	12 45
1·1077	7·30	9 42	10 80	12 90
1 1120	7·55	9 74	11 25	13·35
1·1163	7 80	10 06	11·60	13 80
1 1206	8·22	10 51	12 00	14 30
1 1250	8 50	10 97	12·40	14 80
1·1294	8 84	11·42	12 80	15 25
1 1339	9 18	11 84	13 20	15·70
1 1383	9·49	12·21	13 55	16 10
1 1423	9·80	12·64	13·90	16 50
1 1474	10 15	13 00	14 35	17·15
1 1520	10 50	13 55	14 80	17 60
1 1566	10·82	13 86	15 20	18 10
1 1613	11 14	14 37	15·60	18 60
1·1660	11 43	14 75	16·00	19·05

PERCENTAGES OF CAUSTIC SODA AND CAUSTIC POTASH IN CAUSTIC LYES—*Continued.*

Specific Gravity.	Na_2O. Per cent.	NaOH. Per cent.	K_2O. Per cent.	KOH. Per cent.
1·1707	11·73	15·13	16 40	19·50
1·1755	12 03	15·50	16 80	20·00
1·1803	12·33	15·91	17·20	20 50
1·1852	12·66	16·38	17 60	20·95
1·1901	13·00	16·77	18 00	21·40
1·1950	13 35	17·22	18 40	21·90
1·2000	13·70	17·67	18 80	22·50
1·2050	14·05	18·12	19 20	22·85
1·2101	14 40	18 58	19 60	23 30
1·2152	14 74	19 08	19·95	23 75
1·2202	15 18	19·58	20·30	24 20
1·2255	15 57	20 08	20·70	24 65
1·2308	15 96	20·59	21 10	25·10
1·2361	16·36	21·00	21·50	25·60
1·2414	16·76	21·42	21·90	26·10
1·2468	17 18	22 03	22 30	26 50
1 2522	17 55	22 64	22·70	27·00
1 2576	17·85	23 15	23 10	27·50
1·2632	18·35	23 67	23·50	28 00
1·2687	18 78	24 24	23·85	28 45
1 2743	19 23	24 81	24 20	28·90
1 2800	19 61	25 30	24 60	29 35
1·2857	20·00	25·80	25 00	29 80
1·2905	20·40	26 31	25 40	30 25
1·2973	20 80	26 83	25 80	30·70
1 3032	21·02	27 31	26·25	31 25
1·3091	21 55	27·80	26 70	31 80
1 3151	21 95	28·31	27 10	32·25
1 3211	22 35	28·83	27 50	32 70
1 3272	22 67	29·38	27·90	33 20
1 3333	23 20	29·93	28 30	33 70
1 3395	23 75	30 57	28 80	34 30
1 3458	24 20	31·22	29 30	34 90
1·3521	24·68	31 85	29 75	35 40
1 3585	25·17	32·47	30 20	35 90
1 3649	25 68	33 08	30 60	36 40
1 3714	26 12	33 69	31 00	36 90
1 3780	26 61	34 38	31 40	37 35
1 3846	27 10	34 96	31 80	37 80
1·3913	27 60	35·65	32 25	38 35
1 3981	28·10	36 25	32 70	38·90
1 4049	28·58	36 86	33 10	39·10
1 4187	29 56	38 13	33 95	40 10
1·4267	30·08	38 80	34 40	40 90
1 4328	30·54	39 39	34 90	41·50
1 4400	31 00	39 99	35 40	42·10
1·4472	31 50	40·75	35·95	42 75
1·4545	32 10	41 41	36·50	43 40
1·4619	32 65	42 12	37 00	44 00
1·4694	33·20	42·83	37·50	44 60
1 4769	33 80	43 66	38 00	45·20
1 4845	34·40	44·38	38·50	45·80
1·4922	35 05	45·27	39 05	46·45
1 5000	35 70	46 15	39 60	47·10
1 5079	36·30	46 87	40·15	47 70
1 5158	36 90	47 60	40 60	48 30
1·5238	37·45	48 81	41 05	48 85
1·5319	38·00	49·02	41·50	49 40

Determination by Titration.—For an accurate determination of the percentage of sodium hydroxide, or sodium oxide, present in a sample of caustic soda, a method involving titration should be used. In this case the percentage of sodium carbonate can be ascertained at the same time. The following is a description of the process About 10 grammes of the sample are weighed in a stoppered weighing bottle, and dissolved in water. The solution is washed into a litre flask, diluted to the mark, cooled, and mixed. A portion of the solution, *e g* 50 c c , is transferred to a flask, two or three drops of phenolphthalein solution added, and decinormal hydrochloric acid run in from a burette till the pink colour is just discharged. At this point the whole of the sodium hydroxide will have been neutralised Any sodium carbonate present will have been converted, also, into sodium bicarbonate, as shown by the equations

$$NaOH+HCl=NaCl+H_2O,$$
$$Na_2CO_3+HCl=NaCl+NaHCO_3.$$

Thus, when the pink colour is discharged, the whole of the hydroxide and half of the sodium carbonate will be neutralised. The volume of the acid used having been read off, a drop of methyl orange solution is added to the colourless solution, and the addition of the decinormal acid is continued till the neutral tint is obtained—that is, till the remaining half of the sodium carbonate is neutralised—

$$NaHCO_3+HCl=NaCl+H_2O+CO_2.$$

Evidently, the sodium carbonate present in the 50 c c of the solution titrated must be equivalent to twice the volume of acid used in the second titration, while the volume of acid used in the first titration *less* that used in the second gives the sodium hydroxide, or, if

T=volume of acid used in the first (phenolphthalein) titration

and

t=volume of acid used in the second (methyl orange) titration,

then $2t$ c c corresponds to the sodium carbonate present and $T-t$ to the sodium hydroxide, each cubic centimetre of decinormal acid is equivalent to 0·004 gramme of sodium hydroxide, 0·0053 gramme of sodium carbonate, or 0·0031 gramme of sodium oxide, Na_2O

Winkler's method is also used The total alkali is first determined in a portion of the solution by titrating with decinormal acid in the presence of methyl orange Another portion of the solution is treated with excess of barium chloride solution. This causes the precipitation of any sodium carbonate present as barium carbonate, and changes the sodium hydroxide into soluble barium hydroxide—

$$Na_2CO_3+BaCl_2=2NaCl+BaCO_3,$$
$$2NaOH+BaCl_2=2NaCl+Ba(OH)_2.$$

If some phenolphthalein be added and then decinormal acid is run in slowly with constant stirring, as soon as the barium hydroxide is neutralised the pink colour is discharged This is because the barium hydroxide is neutralised first, and the next drop of acid added liberates carbon dioxide from the barium carbonate, and thus discharges the colour. The volume of acid used in the second titration gives the sodium hydroxide present, and the difference between the two the sodium carbonate

Potassium hydroxide, or caustic potash, KOH, is made from potassium

carbonate or potassium chloride in a similar manner to sodium hydroxide. Like sodium hydroxide it is a white, solid, fusible substance. It deliquesces when exposed to air and absorbs carbon dioxide even more rapidly than sodium hydroxide It saponifies fats more readily than sodium hydroxide Its aqueous solution is strongly alkaline and caustic It is sold in several qualities, viz 75 to 80 degrees and 88 to 92 degrees In this case the degree is the actual percentage of potassium hydrate present The impurities are much the same in nature as those of caustic soda, but are generally rather greater in quantity The following are examples (Hurst, *Dictionary of Chemicals and Raw Products*) —

	1.	2.
Potassium hydrate . . .	77 64	75 64
Potassium carbonate . . .	4 62	2 55
Potassium sulphate	0 38	0 21
Potassium chloride .	2 29	0 93
Potassium nitrite . .	0 87	0 00
Sodium hydroxide .	4 67	2 59
Silica and alumina .	0 30	0 20
Insoluble . . .	0 02	0 22
Water . . .	8 84	17 66

Iron is also a common impurity in the lower grades

Sodium Carbonate, Na_2CO_3, is prepared from sodium chloride by two processes, viz the ammonia and the Leblanc In the former method the solution of salt is mixed with ammonia and subjected to a stream of carbon dioxide gas In this way ammonium chloride and bicarbonate of soda are obtained—

$$NaCl + NH_4OH + CO_2 = NaHCO_3 + NH_4Cl$$

When a concentrated solution is used the sodium bicarbonate, being much less soluble than ammonium chloride, crystallises out The crystals are collected, dried, and heated, when they give up carbon dioxide and water and become changed into sodium carbonate —

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O$$

The Leblanc process consists of the formation of sodium sulphate, its subsequent reduction to sulphide by means of coal and transformation of the sulphide into carbonate by means of chalk

Sodium chloride is treated with the requisite quantity of sulphuric acid, the liberated hydrochloric acid being led into condensing chambers, where it is dissolved in water, and subsequently used for the manufacture of chlorine The following reaction takes place —

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

The sodium sulphate thus produced (termed salt cake) is now ground up, intimately mixed with powdered coal and chalk, and strongly heated in a "reverberatory" furnace Here it is subjected to the direct action of the flames and gases from a large fire, with the result that the sulphate is reduced to sulphide—

$$Na_2SO_4 + 4C = Na_2S + 4CO$$

As the temperature is gradually raised to redness the sodium sulphide and chalk interact with the formation of sodium carbonate—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

The fused mass, which is known as "black ash," is cooled and treated with warm water The carbonate dissolves, and the clear liquid is drawn off, evaporated, and ignited. The product, which is an impure form of sodium carbonate, is known as soda ash. If instead of evaporation and ignition the solution be allowed to crystallise, soda crystals, $Na_2CO_3 10H_2O$, are obtained.

Sodium carbonate is met with in a number of forms, which correspond with different proportions of sodium oxide, Na_2O They are—

Soda ash	48 to 52	per cent. Na_2O.
Pure alkali	57 to 58	,,
Washing soda, $NaC_2O_3 10H_2O$	21 6	,,
Crystal soda, $Na_2CO_3H_2O$	50 0	,,
Sesquicarbonate, $Na_2CO_3 2NaHCO_3 2H_2O$	40 0	,,

Carbonate of soda is generally sold, like the hydroxide, on its sodium oxide value expressed in degrees, *i e* percentage *plus* one

Soda ash is crude, unrefined sodium carbonate It is liable to contain many impurities, such as caustic soda, sodium sulphate, chloride and sulphite, iron oxide and alumina.

Pure Alkali —This is the refined anhydrous sodium carbonate, and it is by far the best form to use, containing from 99 to 100 per cent of anhydrous carbonate of soda, equal to 58 per cent Na_2O, and only traces of impurities.

Washing Soda, or Soda Crystals, $Na_2CO_3 10H_2O$ —These are the common large crystals, which effloresce rapidly on exposure to air The chief impurities are sulphates and chlorides

Crystal Soda, $Na_2CO_3H_2O$ —These are small crystals, and generally purer than the large crystals, owing to the much larger soda content, they are much more economical in use.

Sesquicarbonate of sodium, $Na_2CO_3 2NaHCO_3 2H_2O$, is made by the rapid crystallisation of a solution of sodium bicarbonate which has been heated till it parts with a portion of its carbon dioxide

The following analyses show the composition of some commercial samples –

	48 per cent	58 per cent	Pure Ammonia Alkali	Soda Crystals	Crystal Soda.	Sesqui-carbonate
Sodium carbonate	60 64	98 72	98 94	34 22	81·92	46·62
Sodium bicarbonate						37 30
Sodium sulphate	4 35	0 20	0 20	2·54	0 18	
Sodium hydrate	1 29			0 10	..	
Sodium chloride	28 34	0 54	0 36	0 27	0 24	0 29
Ferric oxide	trace	0 04	...	..	...	...
Alumina	1 12	0 01	.		...	...
Silica	0 00	0 09	0 09	0 03	...	.
Water	4 26	0·26	0 38	62·84	17 66	15 79

Anhydrous sodium carbonate, Na_2CO_3, is a white amorphous substance which melts without decomposition when heated. It dissolves readily in water, and its solution has an alkaline reaction to litmus, phenolphthalein, and methyl orange This is due to hydrolysis with the formation of sodium hydroxide and bicarbonate—

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH,$$

when its solution is concentrated crystals of the formula $Na_2CO_3 10H_2O$ are

obtained These, on exposure to air, effloresce, giving up 9 molecules of water and becoming changed to $Na_2CO_3\,H_2O$ When a solution of sodium carbonate is added to one of a heavy metal the carbonate of the latter is generally precipitated Thus

$$CaCl_2+Na_2CO_3=CaCO_3+2NaCl,$$
$$CuSO_4+Na_2CO_3=CuCO_3+Na_2SO_4$$

Sodium carbonate does not saponify fats, but it is able to neutralise free fatty acids with the formation of soaps Thus, with oleic acid—

$$2C_{17}H_{33}COOH+Na_2CO_3=2C_{17}H_{33}COONa+CO_2+H_2O$$

The analysis of sodium carbonate is carried out by titration in the manner described for sodium hydroxide

Sodium Bicarbonate, $NaHCO_3$ —When carbon dioxide is brought into contact with finely powdered crystalline sodium carbonate, it is absorbed and the bicarbonate is formed—

$$Na_2CO_3\,10H_2O+CO_2=2NaHCO_3+9H_2O$$

It is produced also in the manufacture of sodium carbonate by the ammonia process described above

Sodium bicarbonate is a white substance which is less soluble in water than the normal carbonate One hundred parts of water at 15° C dissolve 9 of the salt Although an acid salt its aqueous solution has a neutral reaction to litmus When heated, or if its solution be boiled, it becomes changed into the normal salt, carbon dioxide being evolved—

$$2NaHCO_3=Na_2CO_3+CO_2$$

Sodium silicate (or metasilicate), Na_2SiO_3, is made by fusing quartz or sand with sodium carbonate—

$$SiO_2+Na_2CO_3=Na_2SiO_3+CO_2$$

Soluble glass, or water glass, is made in a similar manner It has the composition $Na_2O\,2SiO_2$ or $Na_2Si_2O_5$, being the sodium salt of metadisilicic acid $H_2Si_2O_5$ Commercial sodium silicate, consisting of sodium metadisilicate, is a viscous liquid containing varying proportions of silicate and water It dissolves readily in warm water, and its solution has an alkaline reaction due to the liberation of sodium hydroxide by hydrolysis It is decomposed by acids with the liberation of silicic acid, even such weak acids as carbonic acid being able to effect this decomposition at ordinary temperatures At high temperatures, as indicated above, silicic acid can decompose carbonates

When a solution of sodium silicate is treated with excess of hydrochloric or other acid, a gelatinous precipitate or silicic acid, H_2SiO_3, is formed —

$$Na_2SiO_3+2HCl=2NaCl+H_2SiO_3$$

If dilute hydrochloric acid be stirred very cautiously into a solution of sodium silicate, some of the silicic acid remains in solution as orthosilicic acid, $Si(OH)_4$ This acid is formed in accordance with the equation

$$Na_2SiO_3+2HCl+H_2O=2NaCl+H_4SiO_4$$

When the sodium chloride is removed by dialysis a colloidal solution of orthosilicic acid remains in the dialyser The sodium orthosilicate may be prepared from this acid by careful neutralisation with sodium hydroxide When

orthosilicic acid is exposed to air it loses one molecule of water and forms meta-silicic acid—

$$H_4SiO_4=H_2O+H_2SiO_3$$

When ortho- or meta-silicic acid is dried at 100° C it loses most of its combined water, retaining about 13 per cent In this state it is sparingly soluble in water But when dried at a temperature of 500° C the whole of the water is expelled, anhydrous silica being formed—

$$H_2SiO_3=SiO_2+H_2O$$

Sodium silicate increases the detergent action of a solution of soap and is often used for this purpose It is decomposed by the soluble salts of many metals, such as those of calcium and magnesium with the formation of insoluble silicates -

$$Na_2SiO_3+CaSO_4=Na_2SO_4+CaSiO_3$$

Borax, $Na_2B_4O_7\,10H_2O$, is the most important salt of boric acid, H_3BO_3 It may be prepared from boric acid by neutralising a boiling solution with sodium carbonate—

$$4H_3BO_3+Na_2CO_3=Na_2B_4O_7+6H_2O+CO_2$$

The hot solution is allowed to crystallise, when large prisms with the composition $Na_2B_4O_7\,10H_2O$ are obtained Borax is made also from tincal $Ca_2B_6O_{11}$ The mineral is powdered, and boiled with water and sodium carbonate The following reaction takes place—

$$Ca_2B_6O_{11}+2Na_2CO_3=2CaCO_3+Na_2B_4O_7+Na_2B_2O_4$$

Thus, a mixture of calcium carbonate, borax, and sodium metaborate, $Na_2B_2O_4$, is obtained The insoluble calcium carbonate is removed, by filtration, and the hot liquor is then allowed to cool, when the borax crystallises out The mother liquor is concentrated and treated with carbon dioxide, which converts the metaborate into borax, which is precipitated as a fine powder—

$$2Na_2B_2O_4+CO_2=Na_2CO_3+Na_2B_4O_7$$

Borax is a white solid substance, sparingly soluble in water, 100 parts dissolving 4 6 parts of borax at 10° C and 201 4 at 100° C

When its solution is treated with hydrochloric acid, boric acid, H_3BO_3, is liberated—

$$Na_2B_4O_7+2HCl+5H_2O=2NaCl+4H_3BO_3$$

Since boric acid is not acid to methyl orange, borax can be titrated in its presence, and the percentage of alkali (Na_2O) determined If the same volume of standard acid be added to the same volume of the borax solution, and then some phenolphthalein and about 30 per cent of neutralised glycerin, the boric acid can be titrated by adding decinormal sodium hydroxide solution till a faint pink colour is produced The reaction is

$$H_3BO_3+NaOH=NaBO_2+2H_2O,$$

that is, sodium metaborate is produced, and each cubic centimetre of decinormal alkali is equivalent to 0 0062 gramme of boric acid If glycerin be not added, the pink colour appears before all of the boric acid is neutralised, owing to the fact that sodium borate is hydrolysed by water The glycerin inhibits

the hydrolysis. Orthoboric acid, H_3BO_3 or $B(OH)_3$, is a tribasic acid. When it is heated to 100° C. it loses water, forming metaboric acid—

$$H_3BO_3=H_2O+HBO_2,$$

or

$$2H_3BO_3=2H_2O+H_2B_2O_4.$$

Sodium metaborate is a salt of this acid. When boric acid is heated to a temperature of 140° C., tetraboric or pyroboric acid, $H_2B_4O_7$, the acid from which borax is derived, is formed—

$$4H_3BO_3=5H_2O+H_2B_4O_7.$$

When heated, borax loses its water of crystallisation and swells up to an opaque white mass. Further heating causes this to melt. If the melted mass be cooled, a transparent glass-like mass of anhydrous borax is formed. In its melted condition it dissolves many metallic oxides, characteristic colours being produced in many cases This property is made use of in the borax bead test for the metals

Borax is used as a preservative for foods and starch dressings. It is, however, not very powerful, at least 0·5 per cent being required Its solution emulsifies fats and waxes although unable to saponify them. It is what is termed a mild alkali as opposed to strong caustic alkalis

Commercial borax should be free from sulphates and chlorides and all metals other than sodium

The Analysis of Borax.—A weighed quantity of the substance is dissolved in distilled water and made up to a definite volume Twenty-five or 50 c.c. are withdrawn and titrated with decinormal hydrochloric acid, methyl orange being used as indicator. Each cubic centimetre of acid used corresponds to 0·0031 gramme of sodium oxide, Na_2O. Pure borax contains 16·2 per cent. The neutralised solution is boiled for two or three minutes to expel carbon dioxide, and then cooled. About one-third of its volume of glycerin (carefully neutralised with decinormal sodium hydroxide and phenolphthalein) is added, and a drop of phenolphthalein solution.

Decinormal sodium hydroxide is then added till a permanent faint pink colour is produced Each cubic centimetre of acid used corresponds to 0·0062 gramme of boric acid or 0·00955 gramme of crystalline borax.

Ammonia, NH_3.—It has been mentioned that ammonia is produced by the natural decomposition of nitrogenous organic matter under the influence of putrefactive micro-organisms It occurs, therefore, in small quantities in air and water. It may be made by reducing nitrates or nitrites with nascent hydrogen If a solution of sodium nitrate be treated with reduced iron and dilute sulphuric acid, the nitrate is all converted into ammonia, which combines with the excess of sulphuric acid to form ammonium sulphate—

$$8Fe+8H_2SO_4=8FeSO_4+16H,$$
$$2NaNO_3+H_2SO_4=2HNO_3+Na_2SO_4,$$
$$2HNO_3+16H=2NH_3+6H_2O,$$
$$2NH_3+H_2SO_4=(NH_4)_2SO_4$$

These reactions are made use of in the estimation of nitrates, but are not suitable for the preparation of ammonia. It is generally prepared by heating an ammonium salt with a solution of an alkali. Thus, if ammonium chloride be heated with a solution of sodium hydroxide, the following reaction takes place:—

$$NH_4Cl+NaOH=NaCl+NH_3+H_2O.$$

With slaked lime and ammonium chloride the reaction is similar—

$$2NH_4Cl+Ca(OH)_2=2NH_3+CaCl_2+H_2O$$

The chief source of commercial ammonia is gas liquor. When coal is heated in closed retorts, in the manufacture of coal gas, ammonia is produced as one product This, together with other impurities, is removed from the gas by passing it through condensers The coal tar is condensed and also water and ammonia The solution of ammonia containing salts of ammonium and other soluble bodies floats on the tar. It is known as gas liquor When it is heated with lime, ammonia gas is given off. This may be dissolved in water or in sulphuric acid In the latter case ammonium sulphate, $(NH_4)_2SO_4$, is formed

Ammonia is a colourless gas with a pungent smell It is heavier than air, and may therefore be collected by downward displacement. It is very easily liquefied, and the liquefied gas may be obtained in cylinders It boils at —135° C When liquid ammonia is evaporated it absorbs much heat from its surroundings, and for this reason it is used in the manufacture of ice It is extremely soluble in water One volume of water at 0° C and 760 mm pressure dissolves 1298 volumes of ammonia gas Commercial ammonia is simply a solution of the gas in water Ammonia gas may be made from this solution by heating it, the whole being expelled at the boiling-point The specific gravity of a solution of ammonia in water decreases gradually as the percentage of ammonia increases Commercial ammonia has a specific gravity of 0 88, corresponding to about 36 per cent of NH_3 The following table gives the relation between concentration and specific gravity —

AQUA AMMONIÆ

Degrees Baumé	Specific Gravity.	Per cent NH_3	Degrees Baume	Specific Gravity	Per cent NH_3	Degrees Baume	Specific Gravity	Per cent NH_3
10 00	1 0000	0 00	16 50	0 9556	11 18	23 00	0 9150	23 52
10 25	0 9982	0 40	16 75	0 9540	11 64	23 25	0 9135	24 01
10 50	0 9964	0 80	17 00	0 9524	12 10	23 50	0 9121	24 50
10 75	0 9947	1 21	17 25	0 9508	12 56	23 75	0 9106	24 99
11 00	0 9929	1 62	17 50	0 9492	13 02	24 00	0 9091	25 48
11 25	0 9912	2 04	17 75	0 9475	13 49	24 25	0 9076	25 97
11 50	0 9894	2 46	18 00	0 9459	13 96	24 50	0 9061	26 46
11 75	0 9876	2 88	18 25	0 9444	14 43	24 75	0 9047	26 95
12 00	0 9859	3 30	18 50	0 9428	14 90	25 00	0 9032	27 44
12 25	0 9842	3 73	18 75	0 9412	15 37	25 25	0 9018	27 93
12 50	0 9825	4 16	19 00	0 9396	15 84	25 50	0 9003	28 42
12 75	0 9807	4 59	19 25	0 9380	16 32	25 75	0 8989	28 91
13 00	0 9790	5 02	19 50	0 9365	16 80	26 00	0 8974	29 40
13 25	0 9773	5 45	19 75	0 9349	17 28	26 25	0 8960	29 89
13 50	0 9756	5 88	20 00	0 9333	17 76	26 50	0 8946	30 38
13 75	0 9739	6 31	20 25	0 9318	18 24	26 75	0 8931	30 87
14 00	0 9722	6 74	20 50	0 9302	18 72	27 00	0 8917	31 36
14 25	0 9705	7 17	20 75	0 9287	19 20	27 25	0 8903	31 85
14 50	0 9689	7 61	21 00	0 9272	19 68	27 50	0 8889	32 34
14 75	0 9672	8 05	21 25	0 9256	20 16	27 75	0 8875	32 83
15 00	0 9655	8 49	21 50	0 9241	20 64	28 00	0 8861	33 32
15 25	0 9639	8 93	21 75	0 9226	21 12	28 25	0 8847	33 81
15 50	0 9622	9 38	22 00	0 9211	21 60	28 50	0 8833	34 30
15 75	0 9605	9 83	22 25	0 9195	22 08	28 75	0 8819	34 79
16 00	0 9589	10 28	22 50	0 9180	22 56	29 00	0 8805	35 28
16 25	0 9573	10 73	22 75	0 9165	23 04			

ALLOWANCE FOR TEMPERATURE

The coefficient of expansion for ammonium solutions, varying with the temperature, correction must be applied according to the following table —

Corrections to be added for each Degree below 60° F			Corrections to be subtracted for each Degree above 60° F			
Degrees Baume	40° F	50° F	70° F	80° F	90° F	100° F
14°	0 015° Be	0 017° Be	0 020° Be	0 022 Be	0 024° Be	0 026 Be
16	0 021 ,,	0 023 ,,	0 026 ,,	0 028 ,,	0 030 ,,	0 032 ,,
18	0 027 ,,	0 029 ,,	0 031 ,,	0 033 ,,	0 035 ,,	0 037 ,,
20	0 033 ,,	0 036 ,,	0 037 ,,	0 038	0 040 ,,	0 042 ,,
22	0 039 ,,	0 042	0 043 ,,	0 045	0 047 ,,	
26	0 053 ,,	0 057 ,,	0 057 ,,	0 059 ,,		

When ammonia gas is dissolved in water, heat is evolved, while if it be driven out of the solution by a current of air this heat is reabsorbed from the water, thus reducing its temperature When a solution of ammonia in water is frozen, crystals are obtained which are believed to consist of ammonium hydroxide, NH_4OH That is when ammonia dissolves in water a chemical change takes place resulting in the formation of a hydroxide of similar constitution to that of sodium hydroxide —

$$NH_3+H_2O=NH_4OH$$

This is known as ammonium hydroxide, in which the group or radicle NH_4 acts as a monovalent metal

This aqueous solution has both alkaline and basic properties Thus, it turns red litmus blue, and in concentrated solutions has a caustic action When neutralised with acids it gives rise to salts and water in exactly the same manner as sodium hydroxide Thus

$$NH_4OH+HCl=NH_4Cl+H_2O$$
$$2NH_4OH+H_2SO_4=(NH_4)_2SO_4+2H_2O$$

Moreover, if a solution of ammonia in water be added to one containing a salt of a metal which forms an insoluble hydroxide, the latter is precipitated exactly as it would be by sodium hydroxide Thus, with aluminium chloride—

$$Al_2Cl_6+6NH_4OH=Al_2(OH)_6+6NH_4Cl$$

Ammonium salts are produced also by the direct union of ammonia with acids Thus, when ammonia comes into contact with hydrochloric acid gas, dense white fumes of ammonium chloride are produced—

$$NH_3+HCl=NH_4Cl$$

Ammonia is decomposed by chlorine with the formation of nitrogen and hydrochloric acid—

$$2NH_3+3Cl_2=N_2+6HCl$$

The hydrochloric acid unites with the excess of ammonia to form ammonium chloride Further action of chlorine on ammonium chloride results in the formation of a very violent explosive nitrogen chloride, NCl_3

. When ammonia is treated with hypochlorous or a hypochlorite acid, chloramine, NH_2Cl, is produced —

$$NH_3 + NaOCl = NaOH + NH_2Cl$$

The Analysis of Ammonia.—The percentage of ammonia present in a solution may be ascertained with approximate accuracy by taking the specific gravity of the solution and referring to the table given above. The Baumé hydrometer is the only one suitable for liquids which are lighter than water, but a stoppered specific gravity bottle (fig 127) may be used. This is first dried and weighed. It is then filled with the ammonia solution at a temperature of 60° F. till the level of the liquid is exactly at the mark on the neck The stopper is then replaced and the bottle again weighed. It is now washed, filled to the mark with distilled water at 60° F, and weighed From the weights obtained the specific gravity of the ammonia solution can be calculated

Accurate determinations are made by titration with decinormal sulphuric acid About 10 c c of the ammonia solution are weighed in a stoppered weighing bottle, washed into a 500 c c flask with distilled water, the solution made up to 500 c c, and mixed Twenty-five c.c are then withdrawn by means of a pipette and titrated with acid, methyl orange being used as indicator Each cubic centimetre of decinormal acid neutralises 0·0017 gramme of ammonia



Fig 127 — Specific gravity bottle

Ammonia solution should be quite colourless, and leave no residue when evaporated to dryness on a water-bath It contains, occasionally, distinct traces of pyridine This can be detected by its smell after neutralisation with sulphuric acid When excess of nitric acid is added to ammonia solution and then some silver nitrate, the production of a yellow colour indicates, also, the presence of pyridine, while a distinct turbidity or precipitate is produced in the presence of chlorides The formation of a precipitate with barium chloride, after adding excess of nitric acid, would indicate the presence of sulphates Sulphides can be detected with lead acetate paper Ammonium carbonate is tested for by mixing the ammonia solution with an equal volume of lime water and boiling the mixture In the presence of carbonates a distinct turbidity is produced

Pyridine may be estimated by the following method (Grossmann, *Ammonia and its Compounds*, p 56) —

One hundred c c of the solution are neutralised with dilute sulphuric acid and cooled. The solution is then made alkaline with caustic potash and distilled The first third of the distillate will contain all the pyridine present This is mixed with 10 grammes of mercuric chloride, diluted to 400 c c with water, and again distilled. The distillate should not require more than 2 c c. of decinormal soda (0 00948 per cent of pyridine) before becoming neutral to methyl orange

Ammonium Carbonate.—There are three forms of ammonium carbonate, viz —

Normal ammonium carbonate . . .	$(NH_4)_2(CO_3)\,H_2O$
Ammonium bicarbonate . . .	$NH_4\,HCO_3$
Ammonium sesquicarbonate	$(NH_4)_2CO_3\,2NH_4HCO_3$

Commercial ammonium carbonate consists of ammonium hydrogen carbonate with ammonium carbamate, $NH_2\,COONH_4$ It is made by heating a mixture of ammonium sulphate and calcium carbonate It is a white, hard, solid sub-

stance containing about 31 per cent of ammonia When exposed to air it gives off ammonia and is converted into the acid carbonate It is readily soluble in water Ammonium carbonate is determined by titration with standard acid in the manner described for sodium carbonate

Soap.—The term "soap" is applied, in general, to the metallic salts of the higher fatty acids (Chapter VII), and, in particular, to the sodium and potassium salts

Soaps may be prepared from the fatty acids by neutralising them with the hydroxides or carbonates of sodium or potassium Thus, with oleic acid—

$$C_{17}H_{33}COOH+NaOH=C_{17}H_{33}COONa+H_2O,$$
$$2C_{17}H_{33}COOH+K_2CO_3=2C_{17}H_{33}COOK+CO_2+H_2O$$

This process is used commercially Fatty acids are obtained from natural fats, as described in Chapter VII , in three ways, viz —

1 By decomposition by means of superheated steam with or without the addition of sulphuric acid
2 By treatment with Twitchell's reagent
3 By decomposition by means of fat splitting enzymes

The more common method of making soap is by decomposing fats or oils with sodium or potassium hydroxide This operation is termed 'saponification" *When a triglyceride is boiled with an aqueous solution of either of these reagents* it is decomposed, a soap and glycerol being formed—

$$C_3H_5(OOCC_{17}H_{33})_3+3NaOH=3NaOOCC_{17}H_{33}+C_3H_5(OH)_3$$

The sodium soaps are the common hard soaps, the corresponding potassium compounds being termed soft soaps When a fat is saponified, all the products are soluble in the hot mixture The sodium soaps are separated from the glycerol, water, and unused alkali, by taking advantage of the fact that they are insoluble in a concentrated solution of sodium chloride When saponification is complete, salt is stirred into the mixture till the sodium soap becomes insoluble and rises to the surface in the form of a curd This is removed, washed, remelted with a little water, cast into cakes, and dried The brine is clarified by filtration, or by means of charcoal, and concentrated The glycerol is then removed by evaporation, under reduced pressure, the salt being recovered at the same time

Potassium soaps cannot be salted out If salt be added to a solution of a potassium soap, the latter is decomposed, potassium chloride and the sodium soap being formed—

$$C_{17}H_{35}COOK+NaCl=C_{17}H_{35}COONa+KCl$$

As a rule, the mixture of potassium soap and glycerol, produced by saponification, is sold without removing the latter as soft soap But many potassium soaps are made from fatty acids and contain no glycerol The term soft is only a relative one, depending upon the nature of the fatty acids which the soap contains If a hard fat, such as tallow, be used, a comparatively hard soap is produced, though it is always softer than the corresponding sodium compound. Soft soaps contain sometimes white specks termed figs These consist generally of small pieces of potassium stearate, which is a fairly hard soap This appearance is obtained by adding a little tallow to the oil during the saponification White specks may, of course, be due to other causes, such as the presence of starch

Soap-making.—In some bleach works it is the practice to make soaps as required. Having regard to the plant necessary and the question of the disposal

of the by-products, such as glycerin, it is doubtful whether this procedure is economical It is now quite easy to buy soap upon a guaranteed analysis, and competition keeps the prices at a minimum The home manufacture of soap frequently requires a preliminary treatment of the oil with acid This is the case with bone and similar greases, which often contain considerable quantities of lime soaps These cause much trouble in the boiling-pan

In the acid treatment the grease is placed in a lead-lined pan with hot water, sulphuric or hydrochloric acid added, and steam blown through After the grease has been thoroughly washed with the acid, the liquor is drawn off, and the residue washed in the same way with hot water, till all the acid is removed

Soap may be made in several ways, according to the nature of the materials from which it is prepared The following are brief details of the process For fuller details, "Simmons and Appleton's" handbook on soap manufacture should be consulted

The simplest process is from fatty acids These are now prepared on the large scale commercially, and also obtained from recovered grease Fatty acids may be saponified by caustic soda at ordinary temperatures, or by sodium carbonate with the aid of heat Moreover, there is no glycerin to recover The fatty acids are melted and poured slowly, with continual stirring, into sufficient sodium carbonate dissolved in water to completely neutralise them The necessary quantity can be found by a preliminary experiment, but as a general rule, about 19 per cent by weight of the fatty acids taken will be required Pure alkali is generally used, and it is dissolved in sufficient water to make a solution of 58° Tw During the neutralisation of the fatty acids carbon dioxide is given off and the mixture is boiled until this is completely expelled and the solution is clear A little sodium hydrate may then be added to complete the neutralisation of the acid, and, after a little further boiling, the mass allowed to cool, when it is ready for use

The next process, in order of simplicity, is the preparation of soap from readily saponifiable fats, such as cocoanut oil, which contain fatty acids of low molecular weight When this oil is melted out and stirred slowly into a cold solution of caustic soda of specific gravity about 71 4° Tw, and the mixture is allowed to stand, the fats derived from acids of low molecular weight are gradually saponified at ordinary temperatures, and sufficient heat is evolved to complete the saponification of the remainder of the oil A transparent mass of soap is thus obtained The saponification is not, however, generally quite complete, and a certain amount of unsaponified oil and free alkali is usually present, as well as the glycerin originally contained in the oil The soap cannot therefore be used where a neutral product is desired

The most general method of making soaps consists of boiling a neutral fat with caustic soda in an open pan The fat is melted in the pan, and sodium hydroxide solution of 14 to 23° Tw is added, but not at first in sufficient quantity to completely saponify the oil The mixture is boiled gently till saponification commences Successive small quantities of stronger alkali of about 29° to 33° Tw. are now added, and the boiling continued until the fat is completely saponified This is tested by occasionally taking a small quantity from the pan and pressing it between the thumb and finger When sufficient alkali has been used, a firm dry mass is obtained If excess of grease be present, the product will have a greasy feel, and more alkali must be added When this point is reached the boiling is continued for a short time, and if the glycerin is not to be recovered, the mass is allowed to cool As a rule, however, the glycerin is recovered and sold. The separation of glycerin depends upon the insolubility of soap in a solution

of common salt. Instead of cooling the soap, common salt or a brine solution is added while the mixture is still boiling, until a sufficient concentration is reached to make the soap insoluble. This is indicated by the appearance of a sample taken from the pan. When it is seen to consist of two distinct portions, soap and lye, sufficient salt has been added, and the mixture is allowed to cool. As it cools, the soap separates out and floats at the surface, the lye containing the salt, glycerin, and other impurities forming the lower layer. This is drawn off and concentrated to recover both the salt and glycerin. The concentration is best carried out in a vacuum pan; but an open pan is sometimes used, though this causes loss of glycerin. When the lye is evaporated at atmospheric pressure, it is generally placed in a copper, at the bottom of which is a perforated tray which can be removed by means of a pulley. As the lye concentrates, the salt crystallises out, and the crystals are deposited in the tray and removed from time to time. Before concentration, the lye, which contains from about 3 to 8 per cent. of glycerin, is treated with aluminium sulphate and hydrochloric acid to precipitate organic impurities and fatty acids, and allowed to settle or filtered The liquor is then made slightly alkaline with caustic soda, and the precipitated aluminium hydroxide filtered off. The filtrate can be concentrated to a strength of about 80 per cent of glycerin. The product is a brown, viscous liquid, and is sold on its glycerin content

The soap obtained by salting out is now purified in the following manner: After removal of the lye, a little water is added and the mixture boiled till the soap dissolves, and, while boiling, small quantities of soda lye of 32½° Tw are added till no more is absorbed, or until the soap is thrown out of solution. When this point is reached, the mixture is boiled for some time to ensure complete saponification. It is now boiled with steam, and water is added till a smooth paste is obtained, or until a little of the mixture, when removed with a small wooden trowel, drops off in flakes, leaving the trowel clean and dry If too much water be present, it will stick to the wood, and the boiling is continued till the desired consistency is obtained. This process is termed "fitting."

After a further heating the pan is covered, to prevent loss of heat, and the mixture is left for some days to cool slowly. The impurities gradually settle out. The pan is then opened and the soap which is removed is ready for use

If mottled soap be required, the purification need not be carried so far, since mottled soap is essentially soap containing lye, hence impurities

During the resting of the fitted soap the following separations take place At the surface is found a thin crust which is separately skimmed and reboiled. Below this is the soap containing 62 to 63 per cent. of fatty acids Lower down is found a layer of darker and weaker soap termed "nigre," containing only about 33 per cent of fatty acids The quantity of nigre produced depends upon the skill exercised in manufacture It is, of course, an impure soap, and is generally returned to the pan and boiled, and re-precipitated with salt. Below the nigre is a solution containing the saline impurities.

Soft Soap.—This is generally made from either vegetable, fish, or animal oil, with or without the addition of rosin Caustic potash is used for the saponification instead of caustic soda, and no attempt is ever made to recover the glycerin. A small quantity of a solution of about 40° Tw is placed in the pan and boiled; the oil is mixed with a further quantity of lye, and gradually added to the pan with constant stirring As soon as saponification commences the whole of the mixture is quickly added to prevent setting, and the boiling is continued until the mass becomes clear and sets to a jelly when cooled. To obtain a clear soft soap, it is necessary that the lye should contain some carbonate. When the

saponification is complete (tested by observing a sample on a plate), the boiling is discontinued, and the mixture cooled

Rosin Soap.—Rosin is prepared from crude turpentine obtained from pine wood. When this is distilled with steam the turpentine is driven off, and the residue is known as rosin It forms a yellow or brown transparent solid mass which is very brittle and has a melting-point varying from 70° to 140° C. It burns with a yellow smoky flame, producing a characteristic smell. Rosin is insoluble in water, but dissolves in alcohol, ether, and other organic solvents Its solution in alcohol has an acid reaction, and can be neutralised with sodium hydroxide just like a solution of a fatty acid When rosin is boiled with an aqueous solution of sodium hydroxide or sodium carbonate it dissolves, and the solution formed has properties similar to those of a solution of soap

The chief constituent of rosin is abietic acid, $C_{44}H_{66}O_5$ This is monobasic and reacts with sodium hydroxide thus

$$C_{44}H_{66}O_5+NaOH=C_{44}H_{65}O_5Na+H_2O.$$

Rosin soap has very marked detergent properties, and it is often added to commercial soaps for this reason, the rosin being saponified with the fat Rosin soap plays an important part also in the Lancashire system of cotton scouring In addition to abietic acid, rosin contains a variable quantity of unsaponifiable hydrocarbons (from 1 to 15 per cent), which are present also in the soap made from it

The Composition of Soap.—A well-made soap contains about 72 per cent. of true soap and 28 per cent of water Only very small quantities of other bodies are present The impurities include—

1 Unsaponifiable oil or unsaponified triglycerides.
2 Sodium chloride or sulphate
3 Sodium carbonate or hydroxide.
4 Sodium silicate
5 Glycerol

Unsaponifiable oil would be due to the use of an adulterated grease, unsaponified triglycerides to incomplete saponification Salts of sodium, such as chloride, sulphate, carbonate, or silicate, are derived from the caustic soda used, and their presence in the soap is due to the incomplete removal of the lye The same applies to glycerol

Sodium carbonate and sodium silicate are added purposely to soaps. They increase the hardness and, when present in limited quantities, the detergent power also Cheap soaps and soap powders often contain a considerable percentage of sodium carbonate.

Even in the absence of impurities, soap is not a single chemical compound unless it has been made from a pure fatty acid such as oleic acid or stearic acid. When made from fats or oils, it is a mixture of the sodium salts of all the fatty acids present, though one may preponderate The character of the soap depends upon the nature of the glycerides present in the oil from which it was made. The sodium salt of a fatty acid may be represented as a compound of sodium oxide, Na_2O, with the anhydride of the fatty acid The anhydrides of the fatty acids may be produced by the combination of two molecules of the acid with the elimination of a molecule of water. Thus·

$$2C_{17}H_{35}COOH=\begin{matrix}C_{17}H_{35}CO\\ C_{17}H_{35}CO\end{matrix}\!\!>O+H_2O.$$

When the acid anhydride is saturated with a base, a soap results. Thus:

$$\left.\begin{matrix} C_{17}H_{35}CO \\ C_{17}H_{35}CO \end{matrix}\right\rangle O + Na_2O = 2C_{17}H_{35}COONa$$

This reaction is similar to the formation of sodium sulphate from sulphuric anhydride (sulphur trioxide)—

$$SO_3 + Na_2O = Na_2SO_4.$$

The approximate quantity of fatty acid anhydride given by fatty acids is obtained by multiplying the latter by 0·97 The alkali in combination with fatty anhydrides in a soap (or "combined alkali") is expressed as sodium oxide, Na_2O. The combined fatty anhydrides are, however, not determined as such, but as fatty acids. Hence they are generally expressed as such Alkali may be present in soap in at least four forms, viz.—

1 Combined with fatty anhydrides as sodium oxide, Na_2O, to form soap
2 Caustic alkali (NaOH).
3 Sodium carbonate
4 Sodium silicate

The three last named are impurities of either accidental or designed origin. The following table contains analyses of commercial soaps, and shows the variations which may be met with —

	Fatty Acids	Unsaponified Fat.	Combined Alkali.	Free Alkali Carbonate	Titer of mixed Fatty Acids
1. Mottled soap . .	64·06	0·25	8·50	0·50	42
2 White curd . .	62·00	0·25	7·50	0 25	35
3. Olein . . .	65 24	trace	7·59	trace	16·5
4 Vegetable oil . .	64 62	0 10	7 64	0·15	24
5 Olein and tallow .	62 88	0 20	7·00	trace	18 7
6 Soft soap . . .	44·46		9·45	...	12
7 Olein (poor quality) .	61 94	2·09	7 76	0 27	...
8. Tallow . . .	58 75	1·07	6·61	0 28	
9. Do . . .	59 67	...	7 75	3 25	..
10. Powder . . .	85 00	0·25	11 30	0 30	.
11. Do. . . .	51·42	...	6 31	33·18	...

Samples 1 to 5 are good soaps.
Sample 6 is a good soft soap.
Samples 7, 8, and 9 are poor textile soaps.
Sample 10 is a good soap powder.
Sample 11 is a poor powder

Jackson (Cantor Lecture, 1907) gives the following as the chief ingredients of laundry soaps:—

	Oil Soap.		Mottled Soap.		
Fatty anhydrides . .	59 65	66 10	63·24	69 50	70 50
Combined alkali, Na_2O .	7 75	7 65	8·48	9 25	9·50
Free alkali, Na_2CO_3 . .	0 31	1 61	0 40	0 45	trace
Water, etc. . .	32 29	24 61	27 88	20 80	20 00

The same author gives the following illustration of a poor mottled soap:—

Fatty anhydrides	42·41
Combined alkali	4·57
Free sodium carbonate	2·23
Silica	1·56
Sodium chloride	1·24
Sodium sulphate	0·53
Water and insoluble matter	47·46

Types of Commercial Soaps.

There are certain well-defined types of soap used for textile purposes The more important of these are—

Mottled Soap.—This is very commonly made from bone grease, the mottling being due to some of the lye remaining in the interstices of the curd, the impurities which it contains causing the colour Blue and grey mottled soap are coloured by means of ultramarine and manganese dioxide. In addition to bone fat, vegetable oils, such as cotton-seed oil, are used, and sometimes rosin Soaps made from cotton-seed or soya oil are apt to leave a smell if hard water be used, and lime soaps become fixed in the fabric In a well-made mottled soap the percentage of water is never very high, since the foreign matter settles down as the soaps cool, instead of remaining in it But the addition of such bodies as sodium silicate prevents the rapid settling of dirt, etc, and thus sometimes gives the soap a somewhat false appearance Thus, while a good mottled soap always contains 63 per cent of fatty acids, it can be made quite firm and apparently as good and yet only contain 57 to 58 per cent

Curd Soaps—These are largely made from tallow, with, or without, the addition of a vegetable oil, such as cocoanut oil They contain, as a rule, less fatty acid than mottled soaps, the content frequently falling to 60 per cent. The percentage of combined alkali should be small, *i e* from 6·5 to 7 per cent, and free alkali should be entirely absent A little sodium silicate is sometimes present

Oil Soaps—These are generally brown in colour and are made from olein or recovered grease. In the latter case they often contain considerable quantities of unsaponifiable matter A pure olein soap is the best that can be obtained for practically all textile purposes, owing to its ready solubility and high detergent power It should always be examined for unsaponified or unsaponifiable matter.

Vegetable Oil Soaps—This name is given to soaps made from a mixture of vegetable oils with a low titer like that of olein They are therefore somewhat similar to olein soaps, but much cheaper. Olive-oil soap is unsurpassable, but is often adulterated with arachis and other oils. It sometimes consists entirely of foreign oils coloured to simulate olive oil

Desiccated Soaps.—These consist of soap, partly or completely dried, either in the form of flakes or powder The percentage of fatty acids is much higher than in ordinary soaps. Soap powders lend themselves to adulteration. They sometimes contain a considerable quantity of admixed sodium carbonate or other mineral matter.

Sulphonated Soaps—These are compounds of sulphoricinoleic acid. When sulphuric acid is stirred into castor oil, the temperature being kept below 35° C., the oil becomes sulphonated The reaction which takes place is somewhat obscure, but its most important product is sulphoricinoleic acid, $C_{17}H_{32}OSO_2.OH\ COOH$, while some free ricinoleic acid, $C_{17}H_{32}(OH)COOH$, may be formed also. The composition of the final product varies with the quantity of sulphuric acid used and the method of manufacture After the sulphonation is completed the

mixture is poured into a little water and allowed to stand, when it separates into two layers, the upper one consisting of the free fatty acids. The lower layer is drawn off and the fatty acids are washed with a solution of sodium sulphate till the excess of sulphuric acid is removed Sulphoricinoleic acid is soluble in water, and its solution forms a lather in the same way as soap When neutralised with an alkali such as sodium, potassium, or ammonium, hydroxide soaps are formed. These are characterised by great solubility, emulsifying powers, and the readiness with which they wet fabrics. The calcium salts of sulphonic acids are generally soluble in water, and those of sulphoricinoleic acid are no exception. Thus, these soaps do not produce a precipitate with hard water. They are also dissolved by certain organic solvents, particularly in the presence of a fatty acid such as oleic acid. On account of this property they are used largely in the preparation of special scouring or degreasing liquids.

Soft soaps are made, as stated above, from either fatty acids or oils, potassium hydroxide being substituted for sodium hydroxide in the saponification. When they are made from an oil, the glycerol which remains helps to give the soap its characteristic appearance Rosin is sometimes added The percentage of fatty acids is about 45. Potash soaps, if neutral, are always better than the corresponding sodium compounds for textile purposes. There is no better soap than that made from olive oil or oleic acid and potassium hydroxide Those devoid of or containing little glycerol are the best, since glycerol tends to inhibit the detergent action The relative scouring values of sodium and potassium soaps made from oleic acid were determined by the author A constant dry weight of cotton was scoured with equal quantities of each, and, after washing with diluted water, the cotton was dried and weighed and the loss of weight calculated. It was found that, in every case, the potassium soap had removed more than the corresponding sodium soap. From the loss of weight observed, the weight of potassium soap, which removes as much matter as 100 parts of sodium soap, was calculated The results are given in the following table —

Experiment	Sodium Soap	Equivalent of Potassium Soap
No 1	100	72
No 2	100	75
No 3	100	79
No 4	100	84

The Properties of Soap.—Both sodium and potassium soaps are sparingly soluble in cold, but readily soluble in hot, water When a hot concentrated solution of soap in water is cooled it does not crystallise, but sets, forming a jelly which melts again on warming. In this respect it resembles starch or glue and, like these, it is a colloid. Soap dissolves in hot alcohol, but is only very sparingly soluble in other organic solvents, such as ether or petroleum ether.

The lead soaps of oleic acid are, however, soluble in ether, while benzene has the power of dissolving certain soaps, particularly those of the heavy metals.

Ordinary sodium soaps are precipitated unchanged from their aqueous solutions by soluble sodium compounds such as salt. But soaps of different origin require different concentrations of salt solution to cause their precipitation. Thus, cocoanut- and palm-oil soaps are much less readily precipitated than other soaps, and are, on this account, used in the manufacture of marine soaps which give a lather with sea-water

A solution of soap is decomposed by a mineral acid, or by any acid which is stronger than the fatty acid present—

$$C_{17}H_{35}COONa+HCl=NaCl+C_{17}H_{35}COOH$$

If hydrochloric acid be added to a solution of sodium stearate, till the mixture turns methyl orange red, the whole of the combined fatty acid is liberated in the form of a white curdy mass, which melts and rises to the surface if the mixture is heated, forming a clear oily layer

If a solution of soap be treated with a soluble salt of a metal whose soap is insoluble, this insoluble soap is immediately precipitated Thus, with calcium and zinc sulphates and sodium stearate—

$$2C_{17}H_{35}COONa+CaSO_4=(C_{17}H_{35}COO)_2Ca+Na_2SO_4,$$
$$2C_{17}H_{35}COONa+ZnSO_4=(C_{17}H_{35}COO)_2Zn+Na_2SO_4$$

The production of calcium and magnesium soaps has been referred to already as the source of trouble when hard water is used Zinc and other insoluble soaps are sometimes precipitated on fabrics intentionally for the purpose of producing a waterproof finish

When soap is heated it melts, and if the heating be continued takes fire and burns, leaving a residue of sodium carbonate The sodium salts of all organic acids form sodium carbonate when incinerated

The Hydrolysis of Soap.—Many chemical compounds when merely dissolved in cold water are decomposed partly into the hydrates of their constituents This process is termed hydrolysis Soaps possess, to a marked degree, this property of being hydrolysed by water Thus, sodium stearate, when dissolved in water, is partially hydrolysed into sodium hydroxide and stearic acid—

$$C_{17}H_{35}COONa+H_2O \rightleftharpoons NaOH+C_{17}H_{35}COOH$$

It should be noted that some chemists believe that the hydrolysis is not quite so simple as that given in the equation above, but that an acid sodium salt of the fatty acid (or an acid soap) is formed—

$$2C_{17}H_{35}COONa+H_2O \rightleftharpoons NaOH+C_{17}H_{35}COONa\,C_{17}H_{35}COOH$$

Different soaps are hydrolysed to different extents, depending on the nature of the fatty acids they contain It may be stated, as a general rule, that the higher the molecular weight of the fatty acid the more readily do its soaps hydrolyse provided that the fatty acids belong to the same class The amount of hydrolysis which occurs in any particular soap solution depends, also, upon other factors such as (1) the concentration of the solution, (2) its temperature, (3) its state of aggregation As the concentration of the solution decreases, the extent of the hydrolysis increases till a certain dilution is reached, after which the addition of water produces no further hydrolysis Thus, in the case of a particular soap, the volume of decinormal acid necessary to neutralise the alkali liberated from the same weight of soap dissolved in increasing volumes of water at 15° C were—

Dilution	Acid Equivalent of Alkali liberated in c.c. N/10 Solution
1 in 20	1 2
1 in 30	3 6
1 in 40	4 0
1 in 50	4 0

M'Bain (*Reports on Colloidal Chemistry*, 1920, p. 2) states that, in extreme dilution, hydrolysis is very appreciable, but, once the concentration of soap approaches decinormal, the hydroxyl-ion concentration increases, but slowly with further increase of concentration, and passes through a flat maximum shortly before normal concentration is reached The results obtained by E M F in sodium and potassium soaps at 90° C are given in the following table, in which concentrations are expressed in weight normality —

	Sodium Palmitate		Potassium Palmitate	
	OH'	Per cent Hydrolysis	OH	Per cent Hydrolysis
1 0N	0 0020	0 20	0 0008	0 08
0 75N	0 0023	0 30	0 0024	0 31
0 5N	0 0019	0 37	0 0032	0 65
0 1N	0 0013	1 28	0 0013	1 25
0 05N	0 0011	2 22	0 0010	2 02
0 02N		..	0 0011	5 60
0 01N .	0 0007	6 6	0 0007	6 8

The soap solution remains distinctly alkaline even in presence of large excess of palmitic acid Thus, an excess of 10 per cent of palmitic acid only reduced the alkalinity $\frac{1}{5}$th of that given in the table, while when 100 per cent excess was present the OH' is still 0 0004 Thus, only traces of *free* fatty acid can be present in any soap solution, and therefore the effect of hydrolysis cannot be to liberate free fatty acids, but an acid soap intermediate between the neutral soap and the compound $NaHP_2$ where P represents the fatty acid radicle Hydrolysis is diminished, or even inhibited, by the presence of such bodies as alcohol, glycerol, sodium salts, and free alkali If two equal weights of dry soap be placed in separate beakers, and one dissolved in distilled water and the other in an equal volume of a dilute salt solution, it will be found on addition of phenolphthalein, that much less standard acid is required to discharge the colour in the presence of sodium chloride When a certain proportion of salt is present, hydrolysis is inhibited completely, and no pink colour is produced when phenolphthalein is added This seems to throw some light on the use of salt in scouring coloured goods, the liberation of alkali (which attacks the colours) being inhibited, but not the detergent action of the soap

M'Bain and Taylor found that soap solutions are characterised by high electrical conductivity, which indicates that they contain, in addition to neutral colloids, something of the nature of an electrolyte It was established, also, that soap solutions have an osmotic pressure of the same order as that of a non-electrolyte such as sucrose Further, the molecular weight of soap was determined by the dewpoint method (Lewis, *System of Physical Chemistry*, vol II p 326) These experiments indicate that, as the soap solutions become more dilute, there is a gradual transition from colloid to crystalloid Formerly the colloidal solutions, like those of soap, were thought to contain aggregates of undissolved molecules of soap with adsorbed OH ions, giving the aggregate a negative charge M'Bain and Salmon have advanced the micelle theory to explain the phenomena observed Soap belongs to a class of compounds termed colloidal electrolytes These are, according to this theory, salts in which an ion has

been replaced by a heavily hydrated polyvalent micelle, consisting chiefly of agglomerated anions, each micelle carrying an equivalent sum of total electrical charges and conducting electricity as well as, or better than, the simple ion which it replaces. The formula ascribed to this ionic micelle in a soap solution such as one containing sodium palmitate is $(NaP)_x.(P')_n.(H_2O)_m$.

According to this formula (M'Bain), the composition of the micelle must alter continuously with change in concentration or temperature, or upon the addition of salts to the solution. Thus, in very concentrated solutions or in presence of large amounts of another electrolyte, such as sodium chloride or hydroxide, the soap must be nearly all colloid of approximately the composition $(NaP)_x\,(P')_n\,(H_2O)_m$

The molecular weight of the ionic micelle must be at least 3000, although that of sodium palmitate is only 255

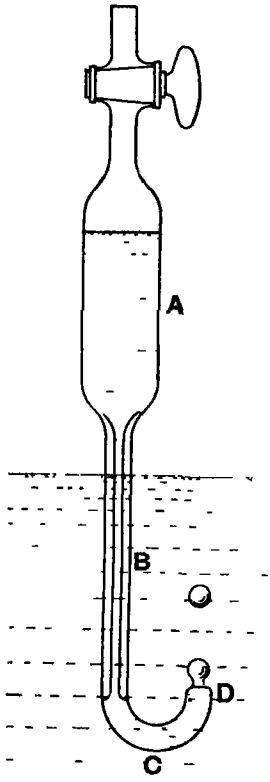


FIG. 128.—Drop-number apparatus.

Lathering Power.—Dilute solutions of soaps, when shaken, form a foam or lather. As a general rule, the more readily a soap forms a lather the better will be its scouring action This property can be measured by determining the volume of a 1 per cent. solution of the soap, which must be added to a definite volume of water to produce a permanent foam, as in the soap test for hardness.

Emulsifying Power of Soap Solutions.—One of the important properties of soap is the power which its aqueous solutions have of emulsifying fats and oils Both oils and fats are insoluble in, and immiscible with, water When oil is shaken with water it becomes separated into globules, but as soon as shaking ceases these rise to the surface and, coalescing, form again a layer of liquid oil. But if a dilute solution of soap be substituted for the water the oil is broken up, on shaking, into very minute globules, which become so intimately mixed with the soap solution that they no longer coalesce readily when shaking ceases, but remain in suspension This intimate mixture of oil and soap solution is termed an emulsion The effect of soap solutions on oil can be studied by the aid of Donnan's "drop-number" apparatus The following description is from Hatschek's *Colloids*, p 38 The apparatus (fig 128) consists of a pipette A, provided with a length of capillary tube B leading to the bend C This is drawn out to a point D, which is ground flat The pipette is filled with the oil and the outlet submerged in the soap solution The oil is then allowed to issue from the pipette, the rate being regulated by means of the tap

If the oil be allowed to flow into water, it will issue in drops. The size of the drop depends upon—

1 The specific gravity of the two liquids
2. The nature and diameter of the orifice.
3 The temperature.

4. The surface tension acting round the circumference of the outlet which tends to retain the drops.

When the oil is allowed to issue into water, a certain number of drops will be formed by the volume contained in the pipette. If water be now replaced by a dilute solution of soap, at the same temperature, the number of drops formed from the same volume of oil will be much greater than when water was used. If more drops are formed each must be smaller also This is because the surface tension acting round the orifice is less The soap solution exercises less tension than the water, *i.e.* the soap has lowered the surface tension between the water and oil. In the case of two immiscible liquids this tension is termed "interfacial" Donnan found that (1) any decrease in this interfacial tension caused a corresponding increase in the "drop number", and (2) the emulsifying power of the soap solution is due to the decreased interfacial tension. Water has a high interfacial tension towards grease and, hence, does not emulsify it; a solution of soap in water has a low interfacial tension towards grease and emulsifies it readily According to Nuttall (*J.S.C.I.*, 1920, 69T), the result of this low interfacial tension is twofold Firstly, the soap becomes concentrated at the surface of the oil globules, and, owing to the surface viscosity produced thereby, the film of liquid intervening between two oil globules resists thinning, and the consequent coalescence of the globules

The second reason why a liquid possessing a low interfacial tension, with respect to oil, should emulsify it, is that the force tending to break the aqueous film intervening between the globules of oil is that of the interfacial tension of the aqueous liquid to the oil, and if this be small, it is not sufficiently strong to withdraw the aqueous film separating the globules. The following experiment is described by Nuttall to illustrate the nature of the film of liquid between adjacent oil globules which resist thinning, and, hence, coalescence of the globules "If a fair-sized bubble of thick mineral oil be placed on the surface of a somewhat concentrated solution of saponin, and, by means of a pipette, saponin solution be introduced into the centre of the floating globule of oil, it is possible to produce a bubble of oil filled with saponin solution, the bubble itself floating in the external saponin solution The thin layer of oil forming the skin of the bubble, whilst, of itself, quite incapable of giving a tenacious film, has become so fortified both internally and externally by the saponin adsorbed on each interface, that a completely rigid structure results This bubble of oil is, in fact, a large-scale representation of the condition of a minute globule of oil in an oil emulsion, except, of course, in the latter case, the globule of oil contains none of the emulsifying agent within itself." Nuttall found that the wetting power of a liquid was also associated closely with its emulsifying power A solution of soap with a high emulsifying power has a correspondingly great wetting power. In the case of textile fabrics this increased wetting power is owing to low surface tension, permitting the liquid to penetrate the capillary interstices.

It is obvious that the soap must be in the form of a solution to exercise its emulsifying powers Hence, for scouring wool, only soaps readily soluble in water at a low temperature, such as sodium oleate, can be used, while with cotton those soluble at a higher temperature are preferred; for example, sodium stearate. Hillyer (*Third Report on Colloidal Chemistry*, p. 16) found that the surface tension of sodium-oleate solutions towards paraffin oil continues to diminish rapidly with increasing concentration up to decinormal. At a temperature of 100° C the curve connecting surface tension and concentration exhibited no

marked difference from that at a lower temperature Rosin soap behaves in the same way as sodium oleate It may be noted that sodium oleate is readily soluble in water Sodium palmitate and stearate, which are soluble only in hot water, were investigated at 70° C and 100° C Hillyer found that traces of these soaps do not lower greatly the surface tension of water towards oil, but as the concentration passes through N/1000 the surface tension falls very rapidly at first, and then above N/180 more gradually up to N/20 solution

It may be noted that decinormal sodium hydroxide has almost as great a surface tension as water Yet oils are emulsified by it This is due, however, to the fact that all triglycerides contain traces or even a considerable quantity of free fatty acids These are saponified by the sodium hydroxide, and the soap produced causes the emulsification of the oil The same is true of sodium-carbonate solutions Shorter, using soap solution and mineral oil, found that the drop number increased rapidly up to a concentration of 0 4 per cent of soap. Further increase in the concentration of the soap solution had little effect, *i e.* there was no further increase in the drop number and consequently in emulsifying power This concentration was not the same for all soaps, but he argues that it is wasteful to use any soap in concentrations above that which has been found by experiment to give the maximum drop number

Shorter's results are not in agreement with those of Hillyer for sodium oleate, since a decinormal solution of this soap would contain nearly 3 per cent

A soap should not only emulsify oil readily, but the emulsion should be fairly "stable" Shorter found that the concentrations giving maximum stability were not the same as those giving the greatest emulsifying power The maximum stability was produced with concentrations of from 0 2 to 0 3 per cent He states also that the presence of small quantities of free alkali in the soap solution increase the drop number, but above a certain concentration diminish the stability of the emulsion formed in the case of mineral oil According to Briggs and Schmidt (*J Phys Chem*, 1915, p 479), the maximum concentration of soap solution for the emulsification of benzene is 1 per cent, while Harkins gives 0 01N The addition of 0 1 per cent of alkali favoured emulsification, but larger quantities decreased the stability It will be observed that there is room for further experiments to clear up some of these points It is, for example, curious, that while drop number determinations appear to indicate that dilute solutions of soap, even at 100° C, have the greatest emulsifying powers, yet in practice concentrated solutions are nearly always used

The Detergent Action of Soap.—Many theories have been suggested to explain the detergent action of soap solutions Dirt is commonly associated with, and, in fact, cemented on to, textile fabrics by means of oil or fat If this fat can be removed, the dirt is often capable of being liberated by merely washing with water or by the action of gravity But some of the dirt is so intimately connected with the fabric as to be incapable, even in the absence of grease, to be removed by simple washing Thus, the soap must do something beyond emulsifying fat or mineral oil

The Hydrolysis Theory —One of the oldest theories of the detergent action of soap is that it is due to the liberation of sodium hydroxide by hydrolysis This liberated alkali was thought to saponify the fat and remove it as soluble soap, the dirt being simultaneously liberated and removed by the motion of the scouring liquor But the quantity of sodium hydroxide which could be liberated by hydrolysis would be much too small to saponify all the fat present, and saponification by such a dilute solution of sodium hydroxide, in the short time during which it could act, would be impossible Saponification by means of dilute

aqueous solutions of either sodium or potassium hydroxide is a very slow process. The saponification of the fatty constituents of cotton requires several hours, even at a temperature considerably above 100° C. But if sodium hydroxide be liberated by hydrolysis, it could neutralise any free fatty acids which were present.

Jackson's Theory of Pedesis.—This is founded on the phenomenon of Brownian movement or pedesis. When finely divided insoluble particles are suspended in water and observed under the microscope, they will be seen to be constantly oscillating. This motion is known as the "Brownian movement" (*vide* Jackson, Cantor Lecture, 1907) or "pedesis." The presence of soap increases the rate of this movement, just as other bodies, such as sulphates, retard it. According to this theory of cleansing, the soap and liberated alkali first saponify or emulsify the envelope of grease which causes the particle of dirt to adhere to a fabric and thus liberates the dirt. This, if sufficiently large or only attached to the surface, is now removed by gravity. If, however, the particles be very minute and entangled within the fibres of the fabric, gravity alone will not remove them. As soon as they are freed from their enclosing greasy envelopes they commence to oscillate, the rate of oscillation being accelerated by the presence of soap, and thus they gradually become removed from the fabric. If this theory be correct, a knowledge of the bodies which either promote or hinder pedesis is of great importance. Caustic soda in small quantities, sodium silicate and carbonate and soap are the chief assistants, while sulphate and chloride of sodium, calcium or magnesium salts, glycerol and other alcohols, exercise a marked retarding effect.

From the results of a number of experiments made in the author's laboratory, it was proved that sodium sulphate or chloride require to be present in considerable quantity to inhibit appreciably the hydrolysis of soap. Thus, in most cases at least, a 1 per cent. solution is necessary. This is much above the quantity likely to be present either in the water or as an impurity of the soap itself. On the other hand, quantities of sodium sulphate which are insufficient to inhibit hydrolysis have a marked effect on the scouring power of a soap. Thus, in one experiment, two equal quantities of the same cotton were boiled with soap solution to which, in one case, 1 per cent. of sodium sulphate had been added. After boiling, the cottons were thoroughly washed, dried, and weighed. It was found that while the soap alone removed 2·13 per cent., in the presence of sodium sulphate only 1·12 per cent. was removed. These experiments indicate that hydrolysis has very little to do with the scouring action of soap, but that pedesis is an important factor.

The Emulsion Theory.—The emulsification of oil by soap solutions has been held for a long time to be an important factor in the detergent action of soap. It has been referred to fully above.

The Colloidal Theory.—It has been mentioned above, that although much of the dirt on fabrics is associated with grease, there is much that is not. It is a matter of experience, for example, that if a piece of dirty fabric be extracted with ether in a Soxhlet extractor and then washed with water, it still retains dirt. If it is now washed with soap and water this dirt is removed. Yet no grease could have been present. Hence, soap must in some way remove dirt which is not associated with grease.

Spring (*J. S. C. I.*, 1909, p. 430, 1910, pp. 99 and 363) attributes the detergent action of soap to the formation of absorption compounds between the soap and the dirt, which are more stable than those existing between the material and the dirt. Thus lampblack can be filtered from water by means of filter-paper, and

the deposit cannot be removed by washing with water alone If, however, lampblack be suspended in soap solution it assumes a colloidal condition and readily passes through filter-paper and loses the power of adhering to it In the same way iron oxide, colloidal iron hydroxide, and silica all form absorption compounds with soap Thus a 1 per cent solution of soap will carry 206 times more clay and 37 times more silica through a filter paper than water alone In using hydrated precipitated silica of the composition $7SiO_2 3H_2O$, Spring found that when this compound was shaken with soap solution the latter was partially split into a more basic and a more acid portion A part of the basic soap was precipitated on the silica, the supernatant liquid containing less ash than the original solution After filtration the solids of the filtrate contained more ash, the quantity increasing with the dilution of the soap solution The absorption compounds are unstable and decomposed by excess of water The rate of settling of suspended silica from a soap solution bears a definite relation to the concentration Thus, with clay, the rate of sedimentation is lowest at a concentration of $\frac{1}{2}$ per cent of soap Beyond this it increases, and at $\frac{1}{4}$ per cent concentration it is very rapid The colloidal theory is supported by the impossibility of cleaning many fabrics without the aid of combined milling and soaping The effectiveness of this operation is most marked after the usual solvents have been applied and have failed to remove the matter entangled in or adhering to the fabric Thus in many cases no grease can be left, so that we must be dealing with some phenomenon of physical solution This is particularly noticeable in the case of blackened stains

It is evident that no one theory can explain completely the detergent action of soap The following conclusions are taken from the *Third Report on Colloid Chemistry* ' It emerges from all this discussion that there are a number of definite factors in detergent action, first, the necessity for having the soap in solution, second, power of emulsification which goes parallel with low surface tension and the formation of surface films, third, wetting power which, like the last, is ascribable to the undecomposed soap itself, fourth, the action of soap in forming non-adhesive colloidal adsorption compounds with tissue and impurities due sometimes to acid soap, but more often to soap itself, and capable of remaining in stable suspension, fifth and lastly, it is an essential in all cases that the soap should be in colloidal form "

The Analysis of Soap.—The analysis of soap includes some or all of the following —

1 The percentage of (*a*) water, (*b*) fatty acids, (*c*) combined alkali, (*d*) free alkali (*e*) unsaponified fat or unsaponifiable oil, (*f*) silica or other mineral impurities

2 The examination of the fatty acids, including the detection and estimation of rosin if present

3 The testing of its detergent action

The following methods may be used —

1 *Water*—About 5 grammes of the sample are cut into fine shavings and weighed in a flat bottomed dish The dish and its contents are dried for some hne at about 40° to 50° C in order to prevent the soap from melting The dish the en placed in an air oven, heated to a temperature of 105° C, and weighed at ing hals till no more weight is lost

hydrol*yatty Acid*s —About 10 grammes of the soap are dissolved in hot distilled cation b The solution is then titrated with normal acid, with methyl orange as which it cid the total alkali present calculated as sodium oxide, Na_2O The

beaker containing the decomposed soap is now placed in boiling water till the fatty acids form a clear layer on the surface. A ribbed filter-paper is placed in a funnel, wetted, and the mixture filtered, care being taken to prevent the fatty acids from solidifying on the filter-paper. If the mixture be kept hot, the fatty acids remain on the paper. They are washed several times with hot water and finally allowed to drain. A flat glass evaporating dish with vertical sides is then placed beneath the filter-funnel, and the fatty acids on the filter are dissolved in hot spirit and collected in the dish. The spirit is then evaporated and the residue dried and weighed.

Alternatively, the soap solution can be washed into a separating funnel, decomposed with acid and extracted with ether, the ethereal solution of the fatty acids being evaporated in a weighed flask. It should be noted that petroleum ether is not a good solvent for some kinds of fatty acids and rosin acids.

The fatty acids obtained by either of these methods include any unsaponified or unsaponifiable oil that may be present.

3. *Combined and Free Alkali.*—About 5 grammes of the sample are cut into flakes and dried at a low temperature. The dry soap is then placed in a ribbed filter paper, and this is extracted with boiling neutral alcohol in a continuous extractor, described on p. 77 The soap and any free sodium hydroxide are dissolved, sodium carbonate and other impurities remaining in the filter-paper. A drop of phenolphthalein solution is added to the alcoholic extract If a pink colour be produced, decinormal acid is added till it is discharged The volume used gives the quantity of caustic alkali present. The alcoholic solution is next evaporated, the residual soap dissolved in hot distilled water and titrated with normal acid and methyl orange. From the volume of normal acid used the combined alkali (Na_2O) is calculated

The residue on the filter-paper is washed with hot water to dissolve sodium carbonate. The combined washings are cooled and titrated with decinormal acid in presence of methyl orange Each cubic centimetre used is equivalent to 0·0053 gramme of anhydrous sodium carbonate

The method just described takes some time to carry out. When only free caustic alkali is required the following is more rapid Ten grammes of the soap are dissolved in about 125 c.c of hot distilled water free from carbon dioxide, and the solution transferred to a 250 c c flask. To this is added a slight excess of barium-chloride solution, say 25 c.c of a 10 per cent. solution. After mixing and adding more barium chloride, if necessary, the contents of the flask are made up to 250 c c. with carbon dioxide free distilled water, mixed and filtered. The extra 10 c c are to compensate for the volume of the precipitate. The whole of the soap will have been precipitated as an insoluble barium compound, while any caustic soda present will have been changed into soluble barium hydroxide—

$$2NaOH+BaCl_2=2NaCl+Ba(OH)_2.$$

If a portion of the filtrate be titrated with decinormal acid, this barium hydroxide, and consequently the original sodium hydroxide, can be calculated. The total free alkali can be determined in a similar manner Ten grammes of the soap are dissolved as before and transferred to a 250 c.c. flask. A hot saturated solution of sodium chloride is then added, in small quantities at a time, to the soap solution with agitation, till the soap is completely precipitated. The mixture is then cooled, made up to 250 c.c. as before, and filtered. Fifty c.c. of the filtrate are then titrated with decinormal acid and phenolphthalein till

the pink colour disappears and does not reappear on boiling. From the volume of acid used the total free alkali (as Na_2O) can be calculated. If free caustic alkali has been determined by the barium-chloride method (as Na_2O) the sodium carbonate may be obtained by difference.

Newington (*J.S.C.I.*, 1916, p. 95) describes the following method Ten grammes of the soap are placed in a 250 c.c. flask and dissolved in 50 c.c. of hot carbon dioxide free water. Fifty c.c of a hot saturated solution of sodium sulphate are added. The mixture is then transferred to a separating funnel, the flask being rinsed with saturated sodium-sulphate solution. The separator is then placed vertically in hot water or a steam-oven till the soap separates and collects at the surface. The lower layer is drawn off and titrated, using spots of silver-nitrate solution on a porcelain plate as indicator As long as any free sodium hydroxide is present brown silver oxide is produced

4 *Free Fat and Unsaponifiable Oil*—A weighed quantity of the soap is cut into thin shavings, dried as described above, and extracted with petroleum ether in a Soxhlet extractor (p 76). After extraction the petroleum ether is poured into a separating funnel and washed once or twice with small quantities of water to remove any dissolved soap The washed extract is then evaporated in a weighed flask and the residue dried and weighed This will include both unsaponified fat and unsaponifiable matter The latter can be determined in this residue in the manner described on p. 264

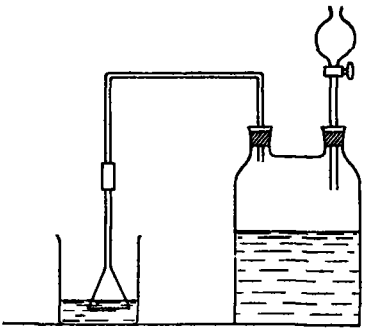


Fig 129 - -Apparatus for rosin acids.

Silica and other mineral impurities are estimated in the ash This, which consists largely of sodium carbonate, is treated with hydrochloric acid The solution is evaporated to dryness, moistened with concentrated hydrochloric acid, again dried, and finally baked or ignited gently on a hot plate The residue is then treated with warm dilute hydrochloric acid and any insoluble silica filtered off, washed, ignited, and weighed

The Examination of the Fatty Acids —Rosin acids are detected in the mixed fatty acids by the following test About 1 gramme is placed in a dry test-tube, a little acetic anhydride added, and the test-tube warmed gently till the fatty acids are dissolved After cooling, the solution is poured into a flat porcelain dish, a drop of concentrated sulphuric acid is then added. If rosin acids are present a violet colour is immediately produced Rosin acids may be estimated by Twitchell's method.

About 3 grammes of the mixed fatty acids are dissolved in 30 c.c. of absolute alcohol, and the solution is subjected to the action of a rapid stream of dry hydrochloric acid gas. For this purpose the apparatus illustrated in fig. 129 may be used. Concentrated hydrochloric acid is placed in the two-holed flask, and strong sulphuric acid is allowed to drop into it slowly from the tap-funnel The solution of the fatty acids is placed in the beaker, and the hydrochloric acid passes in through the inverted funnel This is to produce a larger surface and to prevent the solution from being sucked into the generating flask. The beaker containing the dissolved fatty acids must be cooled by standing it in cold water.

When fatty acids are treated in this manner esters are formed. Thus:

$$C_{17}H_{33}COOH+C_2H_5OH=C_{17}H_{33}COOC_2H_5+H_2O.$$

Rosin acids, on the contrary, remain unchanged.

When no more hydrochloric acid is absorbed, the beaker is covered and allowed to stand for an hour to complete the esterification. Distilled water is then added and the contents of the beaker boiled till most of the hydrochloric acid has been expelled. The mixture after cooling is run into a separating funnel, the beaker being rinsed with ether. More ether is added and the separator is then closed and shaken. The lower layer is run off, and the ethereal layer, which contains both the esters and rosin acids, is washed with cold distilled water. Fifty c c. of a cold 1 per cent solution of potassium hydroxide are then added together with 5 c c of alcohol This will convert the rosin acids into soluble potassium soaps, the esters of the fatty acids remaining dissolved in the ether. The lower solution of rosin soap is run off into another separating funnel Hydrochloric acid is then added, and the liberated rosin acids are dissolved in ether, the ethereal solution transferred to a weighed flask, evaporated, dried, and weighed

The Titer Test—Valuable information about the nature of the fatty acids may be obtained from the results of the titer test A dry test-tube (about 6 cm long and 3·5 cm. in diameter) is half filled with the dried fatty acids. A delicate thermometer, held by a cork, is placed in the tube The fatty acids are melted and then allowed to cool (protected from draughts) until a few crystals are formed at the bottom of the tube The mass is then stirred by means of the thermometer, without allowing it to touch the sides of the tube, in such a way as to incorporate these crystals with the rest of the fatty acids. The cork is then replaced and the thermometer watched carefully. The temperature will continue to fall for a time, but finally will rise and remain stationary for a short time as the fatty acids solidify This stationary temperature is known as the "titer"

Different oils have varying but fairly constant titer values. This is seen in the table. The test is useful for two reasons Firstly, as a general rule, a low titer is accompanied by high solubility of the soap. Secondly, the titer test enables one to judge the nature of the oil from which the soap has been made

Nature of Oil.	Titer of Fatty Acids °C
Olive oil	21
Palm oil	36 to 45
Cocoanut oil	22 to 25
Cotton-seed oil	33 to 45
Arachis oil	24 to 28
Palm-nut oil	23 to 25
Castor oil	2 to 5
Bone fat	40 to 42
Tallow	42 to 45
Skin grease	35 to 38

Iodine Value—This denotes the percentage of iodine which is taken up by an oil or its fatty acids, and is a measure of the unsaturated fatty acids present. The iodine-value test is one of the most important in the examination of oils and fatty acids.

The following solutions are required:—

Iodine Solution (Wijs).—9·4 grammes of iodine trichloride and 7·2 grammes

of iodine are dissolved in separate portions of glacial acetic acid in flasks which are covered to prevent absorption of moisture. When dissolved the two solutions are poured into a 1000 c.c. flask and made up to the mark with glacial acetic acid.

Lewkowitsch recommends the following method of preparation on account of cheapness: Thirteen grammes of iodine are dissolved in a litre of glacial acetic acid and the exact amount of iodine present determined by titration with thiosulphate Washed dry chlorine is now passed through the solution till the original titer is exactly doubled, *i.e.* until all the iodine is present as iodine monochloride, the solution at this point undergoing a distinct change in colour. The solution, having been made in either of the above ways, is titrated with decinormal thiosulphate and its iodine value determined If carefully kept it will remain unchanged for a long time. If only used occasionally it should be titrated each time.

Decinormal sodium thiosulphate solution is made by dissolving 24·8 grammes of the crystalline salt in a litre of water.

Chloroform, or carbon tetrachloride, which must absorb no iodine This is ascertained by mixing equal volumes of the solvent and iodine solution, and after some time titrating the iodine with the thiosulphate solution. The volume of thiosulphate required should be exactly the same as for the iodine solution alone

Starch Solution.—Five grammes of soluble starch are made into a thin paste with water, and poured, with stirring, into 50 c c of boiling water The solution must be freshly made each day

Potassium-iodide Solution—A 10 per cent. solution is used The iodide must be free from iodate, since the latter, when treated with hydrochloric acid, gives free iodine.

Method of Performing Experiment.—From 0·1 to 0 3 gramme of the oil is weighed into a well-stoppered white glass bottle of about 500 c c. capacity and 10 c c of chloroform are added.

Lewkowitsch gives the following quantities as suitable —

Drying or marine animal oils . . .	0 15 to 0 18
Semi-drying oil . .	0 2 to 0 3
Non-drying oil	0 3 to 0 4
Solid oil .	0 8 to 1 0

Twenty-five c c of the iodine solution are then run in from a pipette, the stopper replaced, and the bottle allowed to stand in a dark place for an hour Great care must be taken to always deliver the iodine solution in the same way. If a clear solution be not formed after the addition of the iodine solution, more chloroform is added. If during the experiment the colour becomes light brown, more iodine solution should be added, since the absorption only takes place regularly in the presence of excess of iodine. At the end of an hour 20 c.c. of the potassium-iodide solution are added and decinormal thiosulphate solution run in from a burette until only a faint brown colour remains A few drops of starch solution are now added and the titration continued till the blue colour just disappears. The volume of the thiosulphate solution used, deducted from that required for 25 c c. of the iodine solution, gives the equivalent in thiosulphate of the iodine absorbed by the weight of oil taken for the experiment

The following table gives the iodine values of some of the common oils and of their mixed fatty acids:—

Kind of Oil	Iodine Value of Oil	Iodine Value of Fatty Acids.
Castor oil	83–86	87–93
Olive oil	80–88	86–90
Cotton-seed oil	103–108	111–115
Arachis oil	83–100	96–103
Palm oil	51·5	53·3
Palm-nut oil	13–14	12·0
Cocoanut oil	10·7	
Bone fat	55·5	55·5
Tallow	46–55	55–57
Neatsfoot	69–70	62–63

Detergent Power.—Many methods have been proposed for comparing the detergent power of different soaps.

Donnan's drop-number pipette is quite suitable. Its use depends, as explained above, upon the fact that the emulsifying power of a soap varies with the degree to which it lowers the interfacial tension of water towards grease.

In order to obtain comparable results the conditions of experiment must always be the same. A 0·5 per cent. solution is placed in the beaker and the pipette is filled with kerosin or benzol. The tap is then carefully adjusted so that about four drops per minute issue from the ground end of the pipette. The total number of drops formed by the contents of the pipette is counted. The detergent power of the soap solution varies directly with the number of drops formed. The temperature must be that at which the soap is to be used. Thus, for woollen goods 100° F. would be suitable, but 212° F. would be more appropriate for cotton It is very important that the orifice of a drop-number pipette should be ground perfectly flat and smooth.

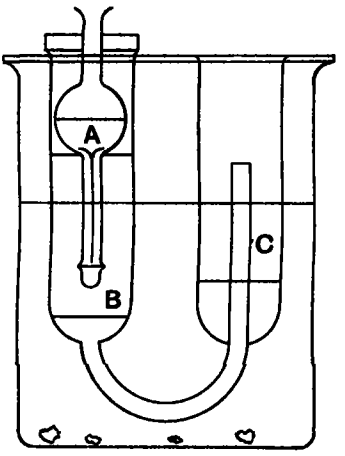


FIG 130.—Hillyer's drop number apparatus.

Hillyer (*Analyst*, 1904, p. 122) recommends the following process His apparatus (fig 130) consists of a pipette A, which holds 5 c.c from a mark on its upper stem to another on the lower capillary outlet tube, the bore of which is 0·5 mm. and which ends in a smooth horizontal surface 10 mm. in diameter from which the drops fall. The stem has a bore of 3 mm., and is widened at its upper end into a small funnel. BC is an oil receptacle. It consists practically of two test-tubes connected by an overflow tube, so that the oil in B can overflow into C, being thus maintained at the same level in B.

In using the apparatus, 2 or 3 c.c. of water are poured into B, followed by 20 c.c. of kerosin. Some of the soap solution to be tested is heated in boiling water, poured into the pipette, and expelled through the capillary by blowing at the other end. After repeating this twice, the pipette is filled with the soap solution, supported by means of cork and dipped into the kerosin. The number of drops formed by 5 c.c. is then counted.

The test may be carried out at room temperature, or any higher, by placing the oil receptacle in a beaker of water at the required temperature.

Two tests are required—

1 *Hot Test* - A 0·5 per cent solution of sodium palmitate is used as the standard for comparison This is prepared by dissolving 0·921 gramme of palmitic acid in 36 c c. of decinormal sodium hydroxide and diluting to 200 c.c. with water Of this solution, 10 c c , 20 c c , 30 c c , and 40 c.c are diluted to 50 c c with boiling water The number of drops formed by 5 c c of each of these solutions, as well as by the undiluted standard, is counted, the results being plotted on a curve

2 *Cold Test* —A similar curve is plotted, using 1 gramme of a 0·5 per cent. solution of sodium oleate as the standard and diluting in the same way. This solution is made by dissolving 0 927 gramme of oleic acid in 32 9 c c of decinormal sodium hydroxide solution and diluting to 200 c c with water. In order to value a soap by means of the hot test, 0·5 gramme of the sample is dissolved in 100 c c of hot water, and the number of drops formed at 100° C by 5 c c is counted The result in terms of sodium palmitate is then read off from the curve

For the cold test, 0·5 gramme of fine shavings are allowed to stand overnight with 100 c c of cold recently boiled water The solution obtained is stirred and filtered through a dry filter-paper in a covered funnel, collecting all that will run through The filtrate is then stirred gently, and 5 c c tested as above and compared with the sodium-oleate standard.

M'Bain, Harborne, and King (*J S C I*, 1923, T. 373) propose to measure the detergent power of a soap by estimating the quantity of finely divided carbon which its solution will carry through a filter-paper The carbon may be weighed or determined colorimetrically by comparison with a special dye solution made by the British Drug Houses, Ltd The "carbon number" obtained in this way may be taken as a measure of the detergent action of the soap solution "Auk" carbon black and *Whatman No* 31 filter-paper are used The method recommended for the colorimetric process is as follows One gramme of the carbon black is placed in a large test-tube with 20 c c of the soap solution, shaken thoroughly and allowed to stand for twenty-three hours at a fixed temperature, then again shaken and allowed to stand for another hour. The mixture is then poured on a 11 3 cm *Whatman No* 31 filter-paper, the filtration being carried out at the same temperature as the digestion. Ten c c of the filtrate are collected and diluted to a known volume with alcohol The specification of the standard dye solution used is 50 c c of nigrosine solution of concentration 0 056 gramme per litre, 20 c.c of Bismarck brown solution (0·0858 gramme per litre), 100 c c of distilled water The light transmitted by this solution is the same as that of the filtrate from a soap with a carbon value of 1·19 In order to obtain the carbon number of any commercial soap it is only necessary to compare the filtrate, after diluting "10" grammes to 100 c c. with alcohol, with the standard dye solution and apply the formula

$$C=1{\cdot}19\frac{l_s}{lw}.$$

l_s and l are the lengths of the columns of standard liquid and filtrate respectively, and w is the weight of the filtrate which has been diluted to 100 c c with alcohol This test is based upon the observations of Spring referred to above. Attempts have been made also to measure the detergent power of soap

by an actual washing test on a piece of soiled fabric under standard conditions. Heermann's test (*J S C.I*, 1921, 176A) may be taken as an example.

The fabric is artificially soiled by immersion in a 0·5 per cent. solution of 20 per cent colloidal indigo paste, pressed until it contains its own weight of liquor, and dried at the ordinary temperature It may be further similarly treated with starch paste and a solution of machine oil in benzene or ether. Samples of the soiled fabric (10 grammes) are cleansed by squeezing twenty times at room temperature in 250 c c of water, of 0 4 per cent. solution of sodium carbonate, of 0·4 per cent solution of soap powder, or of a solution containing 0 125 per cent of palm-oil soap (60 per cent fat), and 0·075 per cent of sodium carbonate The liquor, contained in a porcelain dish, is heated on the water-bath in from ten to fifteen minutes to 50° C and the fabric again squeezed twenty times The dish is then removed from the water-bath, and after each of three intervals of fifteen minutes the fabric is squeezed twenty times (100 times in all), washed in lukewarm water till no more colour is extracted, washed in cold running water, dried, and pressed with a hot iron (sublimation of the indigo must be avoided) Washing must always be carried out with distilled water. The liquids mentioned have an increasing cleansing power in the order given, and for the last this is considered to be 100 Samples of the artificially soiled fabric are cleansed, in the same manner, in solutions of the detergent under examination and then compared with the standards The degree to which a fabric has been cleansed is judged from its colour, and not from its loss in weight. The results obtained by this method are said to agree with those obtained in large-scale practice

CHAPTER XX.

ORGANIC SOLVENTS.

ORGANIC solvents are liquids which have the power of dissolving oil and wax, are not decomposed when boiled, and are without deleterious action on the fabric to be extracted. Commercial solvents must be comparatively cheap and obtainable in large quantities These solvents are used not only in degreasing plants, but also in conjunction with soap, for removing localised grease patches, and in the preparation of levelling or capillarising solutions used in dyeing.

There are several distinct types of solvent used for these purposes, including—

1 Petroleum hydrocarbons of comparatively low boiling-points, consisting chiefly of aliphatic hydrocarbons with the general formula C_nH_{2n+2}

2. Coal tar or aromatic hydrocarbons, such as benzol, C_6H_6

3 Chlorinated hydrocarbons of either aliphatic or aromatic origin

4. Hydrogenated hydrocarbons and their derivatives.

A few particulars of these may be given

Petroleum Hydrocarbons.—These are obtained from American or other petroleum, being the fraction termed light petroleum referred to on p 69 The terms solvent naphtha, benzene, or petrol, or simply spirit, are all used rather indiscriminately for a mixture of hydrocarbons boiling from about 80° to 150° C , and whose specific gravity ranges from 0·65 to 0 75 These are all colourless, inflammable liquids, which are insoluble in, and immiscible with, water The readiness with which they take fire depends upon the proportion of hydrocarbons present with low boiling-point As a general rule, it is advantageous to have as short a range of boiling-points as possible. If the mean boiling-point is below 100° C the goods must be dried before degreasing, with a boiling-point above 100° C they become dried gradually during extraction by evaporation of the water which they contain But a solvent with a very high boiling-point is difficult to recover from the degreased goods, and there is in consequence some loss.

The following table illustrates the differences met with in commercial samples —

	1	2	3	4
Fraction up to 70° C	2 5	1 0	0·0	2 0
„ from 70° to 80° C	21 5	2 0	25 0	4 0
„ „ 80° to 90° C .	31 0	12 0	33 0	14·0
„ „ 90° to 100° C	24 0	82 0	16 0	33 0
„ „ 100° to 110° C.	13 0	3 0	14 0	26 5
„ above 110° C .	8 0	0 0	12 0	20 5

The saturated hydrocarbons, like the paraffins and naphthenes, do not dissolve in sulphuric acid, nor are they decomposed by nitric acid. They give rise to substitution compounds when treated with chlorine, hydrochloric acid being liber-

ated. Thus, methane gives four substitution products, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. The last, carbon tetrachloride, CCl_4, is also an important solvent.

Benzol, also called benzene, is obtained from the first fractions collected in the distillation of coal tar. When coal tar is distilled, it is separated at first into four fractions, viz.—

(1) Light oil or crude naphtha, boiling-point up to 170° C.;
(2) middle oil or carbolic oil, boiling between 170° and 230° C.;
(3) heavy oil or creosote oil, boiling between 230° and 270° C.,
(4) anthracene oil, boiling above 270° C.,

and pitch is left in the retort.

The first fraction contains many bodies, including water It separates into two layers (*a*) gas liquor, and (*b*) light oil, which floats on the surface of the aqueous gas liquor. The light oil, when redistilled, is separated into three fractions, collected between the following temperatures. (1) 82° to 110° C.; (2) 110° to 140° C.; (3) 140° to 170° C. These consist of aromatic hydrocarbons, together with some phenols and aromatic bases, such as pyridine. The latter are removed by washing with sulphuric acid, and the former by means of sodium hydroxide. The washed residues are again distilled. The distillate from the first fraction consists chiefly of benzene, C_6H_6, and toluene, C_7H_8, and constitutes "90 per cent. benzol." The second fraction gives "50 per cent. benzol," consisting of benzene, toluene and xylene, C_8H_{10}. From the third fraction is obtained "solvent naphtha," which consists of xylene and higher homologues of the same series of hydrocarbons.

Benzol containing from 95 to 98 per cent. of benzene, C_6H_6, is also a commercial article.

Benzol is sometimes partly or entirely replaced by petroleum naphtha. Pure benzol is prepared from the commercial substance by freezing, separating the crystals, and redistilling them.

Pure benzol is a colourless liquid which is lighter than water and has a characteristic smell It is inflammable, and boils at 80·5° C It is unchanged when heated with alkalis, but is decomposed by concentrated sulphuric or nitric acids, forming benzene, sulphuric acid, or nitrobenzene—

$$C_6H_6+H_2SO_4=C_6H_5HSO_3+H_2O,$$
$$C_6H_6+HNO_3=C_6H_5NO_2+H_2O.$$

When treated with chlorine in the presence of a chlorine carrier, such as iron, chlorobenzene, C_6H_5Cl, is formed—

$$C_6H_6+Cl_2=C_6H_5Cl+HCl.$$

This is a liquid which boils at 132° C. and is used as a solvent. Commercial benzol consists, chiefly, of benzene, C_6H_6, but may contain toluene or xylene. A constant impurity is thiophene, C_4H_4S. Its presence may be detected by shaking the sample with a little concentrated sulphuric acid and a trace of isatin, when a blue colour is produced. All commercial benzols contain about 0·5 per cent. of thiophene. The presence of any large proportion of toluene is indicated by the raising of the boiling-point, that of toluene being 111° C

Benzene and aromatic hydrocarbons can be distinguished from petroleum products (*i.e.* aliphatic hydrocarbons) by the fact that they give sulphonic acids or nitro compounds, while the paraffin and similar hydrocarbons do not.

Lunge's method of estimating benzol is based on this fact. A qualitative test may be made in the following manner. A little concentrated nitric acid is

mixed with its own volume of strong sulphuric acid in a small flask After cooling the mixture, from 5 to 10 c c of the sample are added, drop by drop, with constant shaking. The mixture is warmed on the water-bath for a short time and then poured into excess of cold water If the sample contains benzol, drops of nitrobenzene, $C_6H_5NO_2$, will settle down to the bottom of the vessel. These can be separated and identified by their smell, or by converting into aniline by warming with tin and hydrochloric acid and then adding excess of sodium hydroxide

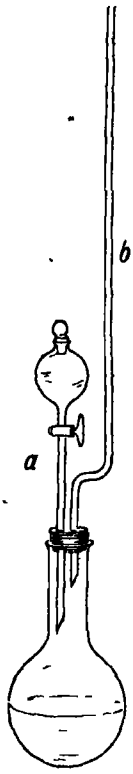


Fig 131.—Estimation of benzol

The following method for the quantitative estimation of benzol may be used. A flask is fitted with a cork, through which pass a stoppered tap-funnel and a long tube to act as condenser (fig 131). One hundred c c of the sample are placed in the flask, which has about 500 c.c. capacity A mixture of 150 grammes of nitric acid (sp gr 1·4) and 180 to 200 grammes of sulphuric acid (sp. gr 1·84) is prepared and cooled This mixture is placed in the funnel and introduced into the flask in small quantities with continual shaking, the flask being at the same time kept cool, if necessary by immersion in water When addition of acid produces no further rise of temperature, the flask is connected to an inverted condenser and gently heated for an hour After cooling, the mixture is poured into a separating funnel and the nitrobenzene separated The acid layer is diluted with water, and any further nitrobenzene which separates added to the rest The crude nitrobenzene is washed with dilute sodium hydroxide and water The washed nitrobenzene is allowed to settle, carefully separated, and redistilled in a fractioning flask until a temperature of 150° C is reached The distillate is again nitrated, using a large excess of the acid mixture. Any material remaining undissolved is non-nitrifiable hydrocarbon 157·6 parts of nitrobenzene correspond to 100 of benzene

The most important test in the case of either benzene or a petroleum solvent is a fractional distillation This may be carried out by the following method (Trotman, *J S C I*, 1906, p 1202) A round flask of 150 c c capacity, and having a neck about 3 inches in length, is fitted to a Young's rod and disc fractionating column, containing sixteen chambers, the distance from the neck of the flask to the lateral exit being 13 inches (fig 132) The thermometer bulb is placed about 1 inch below the lateral tube, which is connected to a Liebig condenser, with an adapter leading into a graduated 100 c.c cylinder One hundred c.c of the benzene are placed in the flask, which is then connected up and placed on a piece of asbestos with an annular hole about 1 inch in diameter. The liquid is heated with a small Bunsen burner protected by a shade, the height of the flame being regulated by means of a screw clamp The distillation is conducted at the rate of about 2 drops a second and the readings taken at intervals of 10° C. The distillation is started with a flame sufficiently large to give the required rate of distillation, and is only altered when either this, or the temperature, shows any signs of falling The distillate is collected in a graduated glass cylinder, which should be stood in cold water of the same temperature as the benzene when measured into the flask. The volume of the distillate is read at each ten degrees, including in the reading all that will come over at that particular temperature It is

convenient to commence reading at 70° C, and to continue at intervals of 10° C up to 110° or 120° C In each case the reading is taken the moment the mercury thread appears above the mark Having obtained these volumes, it is easy to obtain the fraction distilling between each successive 10° C Thus

Volume at 80° C	20
Volume at 90° C	55
fraction distilling between 80° C and 90° C equals	35

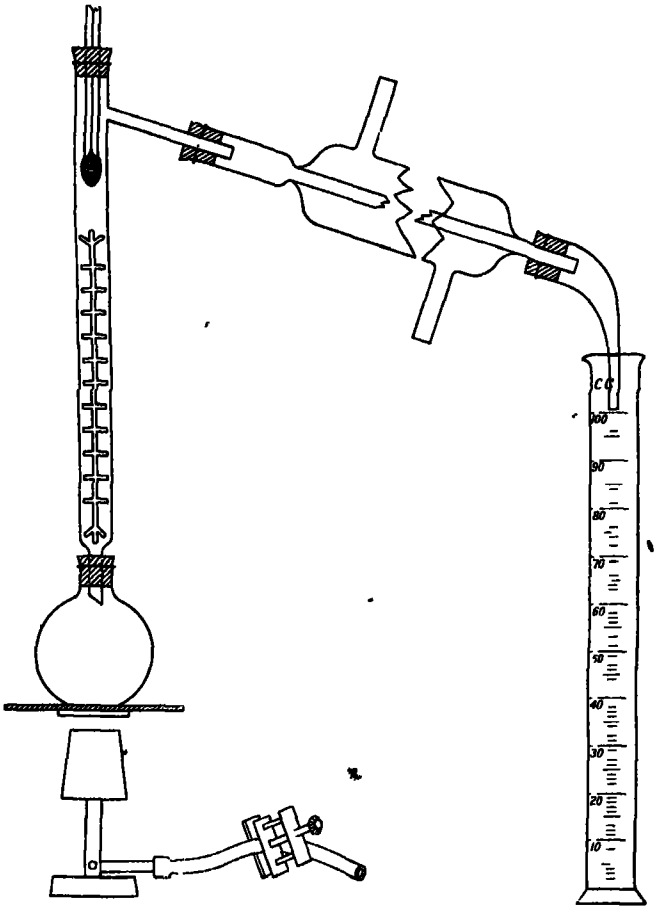


FIG 132.—Distillation apparatus for benzene.

Other tests of importance are—

Specific Gravity.—This should be determined by means of a Sprengel tube

Vapour Tension.—According to Wood (*J S C I*, 1904, p 703), the amount of incondensable vapour in a large plant depends directly upon the vapour tension of the spirit used, and hence the smaller the vapour tension the less spirit is lost The relative vapour tensions of two samples can easily be determined by introducing a few drops of each sample into barometer tubes filled with mercury and noting the depression of the mercury column under identical conditions.

Chlorinated Hydrocarbons.—The simplest of these is carbon tetrachloride,

CCl_4. It is made by passing a mixture of chlorine gas and carbon bisulphide vapour through a heated tube, or by passing the chlorine into boiling carbon bisulphide containing a little iodine—

$$CS_2+3Cl_2=CCl_4+S_2Cl_2.$$

The chloride of sulphur, which is, like carbon tetrachloride, a liquid, is removed by treating the mixture with sodium hydroxide and water, when the following changes take place :—

$$(1)\ 2S_2Cl_2+2H_2O = SO_2+4HCl+3S.$$
$$(2)\ SO_2+4HCl+6NaOH=2NaCl+Na_2SO_3+5H_2O$$

The carbon tetrachloride is then separated, dried, and purified by distillation. It is a colourless liquid with a specific gravity of 1 631, and boiling at 76° C. It has a characteristic smell somewhat like that of chloroform, and, like chloroform, it has anæsthetic properties. Its vapour is non-inflammable. It is an excellent solvent, but is subject to one disadvantage. When its vapour is heated with a caustic alkali or even with water, it is decomposed with formation of carbon dioxide and either sodium chloride or hydrochloric acid—

$$CCl_4+4NaOH=CO_2+2H_2O+4NaCl,$$
$$CCl_4+2H_2O=CO_2+4HCl$$

The tendency to decompose in the presence of water with the liberation of hydrochloric acid makes carbon tetrachloride liable to cause corrosion of metallic vessels. The other chlorinated hydrocarbons used as solvents are derived chiefly from ethane, C_2H_6, and ethylene, C_2H_4, or acetylene, C_2H_2. All of these are, like carbon tetrachloride, definite compounds with a constant boiling-point. They are prepared by treating the hydrocarbons with chlorine under suitable conditions The chlorethanes are substitution products, while the chlorethylenes and acetylene derivatives are addition compounds. This is illustrated by the equations

$$C_2H_6+Cl_2=C_2H_5Cl+HCl,$$
$$C_2H_4+Cl_2=C_2H_4Cl_2.$$

The following table includes the more important of these solvents, excluding carbon tetrachloride, manufactured by the Weston Chemical Co , Ltd. —

TABLE OF CONSTANTS

Name	Dichlor-ethylene	Trichlor-ethylene	Perchlor-ethylene.	Sym Tetra-chlor-ethane	Penta-chlor-ethane.	Hexa-chlor-ethane
Formula	$C_2H_2Cl_2$	C_2HCl_3	C_2Cl_4	$C_2H_2Cl_4$	C_2HCl_5	C_2Cl_6
Molecular weight .	90 9	131 4	165 8	167 8	202 3	236 7
760 mm .		87°				
Boiling-point .	about 52°					
738 5 mm .	..	85°	119°	144°	159°	185° subl
Vapour pressure at 20° C	205 mm	56 mm	17 mm	11 mm	7 mm	3 mm.
Specific heat at 20° C .	0 270	0 223	0 216	0 268	0 266	
Latent heat (calc)	71 Cal	56 59 Cal	51 59 Cal	54 43 Cal.	43 64 Cal	
Coefficient of expansion	about 0 0013	0 001193	0 001078	0 000998	0 000909	
Freezing-point °C.	..	- 73°	-19°	-36°	-22°	
Specific gravity 15° C. .	1 278	1 471	1 624	1·6011	1 685	2 09

These compounds are all non-inflammable, but their vapours have anæsthetic properties. They are heavier than water, having a range of specific gravities from 1·278 to 2·09. Dichlorethylene does not possess a constant boiling-point, since it is a mixture of two isomeric dichlorethylenes boiling at 48° C and 60° C. respectively Chlorinated hydrocarbons have a tendency to decompose when heated with caustic alkali or steam in a similar manner to carbon tetrachloride. Dichlorethylene is said to possess the greatest stability in this respect. Trichlorethylene and tetrachlorethane are sold under the proprietary names of westrosol and westron respectively.

Chlorinated aromatic hydrocarbons, such as monochlorobenzene, C_6H_5Cl, have also a limited use as solvents. This is a colourless liquid, heavier than water, with a boiling-point of 132° C. It is not decomposed by either steam or alkalis. Chlorinated hydrocarbons can be distinguished from hydrocarbon solvents by their smell and by the fact that they are all heavier than water If a few drops of the liquid are warmed gently in a test-tube with a clean shaving of metallic sodium the chlorine is changed into sodium chloride. If the residue is extracted with distilled water, made acid with nitric acid, and some silver nitrate solution added, a white precipitate of silver chloride is produced.

Hydrogenated Hydrocarbons.—These are made chiefly from benzene, C_6H_6, and naphthalene, $C_{10}H_8$, by passing their vapour, mixed with hydrogen, over a metallic catalytic agent, such as nickel, at a suitable temperature Benzene and naphthalene treated in this way give hexahydrobenzene and tetrahydronaphthalene respectively—

$$C_6H_6+H_6=C_6H_{12},$$
$$C_{10}H_8+4H=C_{10}H_{12}.$$

Tetrahydronaphthalene is known as "tetralene." These hydrogenated hydrocarbons are colourless liquids, heavier than water and excellent solvents. Hydrogenated phenols and cresols are also known, and are used in the preparation of detergent soap solutions. "Hexalin" and "methylhexalin" (*J Soc Dyers and Col*, 1923, p 365) are obtained by hydrogenating phenol and cresol, and possess the characteristics of an alcohol with a high molecular weight Their formation may be represented thus:

$$C_6H_5(OH)+3H_2=C_6H_{11}OH,$$
$$C_6H_4(CH_3)OH+3H_2=C_6H_{10}(CH_3)OH.$$

These solvents readily dissolve fatty acid soaps (*i.e.* soap mixed with a free fatty acid), forming clear solutions possessing very marked detergent properties, dissolving calcium and magnesium soaps. It is said that the emulsions of hexalin soap and mineral oil, containing 50 per cent. of the latter, can be washed out of woollen goods in a few minutes at ordinary temperatures.

Solvent.	Boiling-point ° C.	Specific Heat.	Latent Heat Cal grms.	Price per Gallon
				s. d.
Ether . . .	34 6	0 53	90 0	4 0
Carbon disulphide .	46 2	0 24	83·8	3 7
,, tetrachloride .	76 7	0 20	51·0	6 2
Benzol (pure) .	80 3	0 41	93 4	1 7
,, (commercial) .	79–125	0 408	95 0	1 3
Trichlorethylene . . .	87	0 233	56 6	5 3
Petroleum spirit . . .	100–120	0 425	73 5	1 6
Toluene	110 8	0 404	..	1 10

Brewis (*J S C I*, 1924, p 117) gives the foregoing comparative details of some common solvents

The Apparatus used for Degreasing Cotton.

Industrial degreasing plant is constructed generally upon the principle of either the Soxhlet or the continuous extractor used in the laboratory An extraction plant must include a still for the recovery of the solvent and provision for a current of steam, or a hot, non inflammable gas, such as carbon dioxide, to remove the residual solvent from the treated goods

The Arlington process (*J Soc Dyers and Col*, 1921, p 235) is simple A kier of 1000 lbs capacity is employed, which is packed with the goods, filled with solvent naphtha and closed After solution of the grease, the solvent is run off and that remaining in the goods washed out with hot water The kier is then opened and the goods are unpacked and washed

Hey (*J Soc Dyers and Col*, 1919, p 15) recommends Smith's system, of which he gives the following description The apparatus consists of an outer iron casing to contain the solvent, and an inner steel case with a periphery of perforated plates to hold the material to be extracted The cage is carried on a strong steel shaft, and can be made to revolve in the solvent at any desired speed It is divided, radially, into four compartments, each with a door at the periphery, which can be brought opposite to another in the casing The construction of the machine enables centrifuging to be done much more efficiently than with an ordinary hydro-extractor

Valves and pipes are arranged, connecting the extracting chamber with storage tanks for clean, grey, and dirty solvent The drying arrangement consists of large pipes, or ducts, leading from the top of the machine to a cooler, and then through a centrifugal air-tight fan to a heater, and from this to the centre of the apparatus, where the hot gases are distributed through the material in the drying process The material is placed in the cages, through the outer door of the casing This is then closed and made air tight, the pressure reduced by means of a pump, and the hot solvent run in Inert gas, such as carbon dioxide, is led in till atmospheric pressure is reached The cage is rotated slowly in the solvent for a sufficient time to dissolve the grease It is then stopped and the outlet valve connected with the dirty tank is opened The solvent runs away and an equivalent volume of inert gas is drawn in through the delivery pipes and from the dirty storage tank The machine is then run at high speed to remove the solvent as completely as possible by centrifugal action The lower valve of the storage tank is closed, and, if necessary, the operation is repeated with fresh solvent The drying is carried out by starting the fan, which circulates the inert gas through the heater, the materials in the machine, and the condenser The drying is continued until the absence of solvent at the sight-glass shows that the material is dry The doors are then opened and the goods removed in a hot, dry condition, or they may be first cooled by a current of cold gas The impure solvent can be used again or pumped to the still for purification, and the distillate returned to the clean storage tank The dirty solvent can be drawn up to the still by means of the vacuum pump, and that in the vacuum receiver removed by a special ram pump attached to and worked by the vacuum pump Any variation of pressure in the system is compensated or adjusted by the egress or ingress of the atmosphere at the outlet condenser and trap

Coghlan's degreasing plant, shown in fig 133 (British Pat 170645, 1921), has good points, and is suitable for ethylene trichloride 1, 2, 3, 4 are tanks in

which wire cages holding the wool are placed. These are connected by valves *a* to a vacuum pump at *e*. The solvent is contained in the reservoir *f*. From this it is run into tank 1 at a temperature of 45° C., and, after fifteen minutes, from

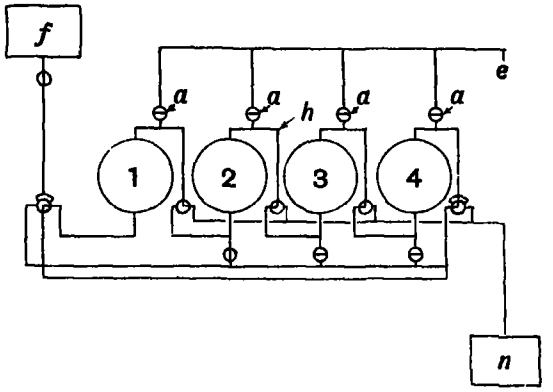


FIG 133 —Coghlan's degreasing apparatus

tank 1 into tanks 2, 3, and 4 successively, and finally from tank 4 into the recovery tank *n* Any tank may be filled with clean solvent from the reservoir *f*

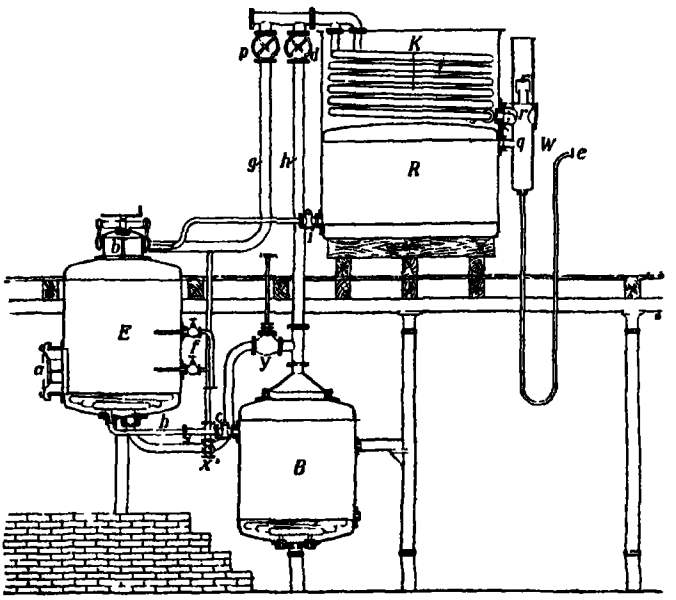


FIG 134 -- German degreasing plant

After the extraction is completed and the solvent has drained into the recovery tank *n*, that which remains in the wool is recovered by means of hot water or a stream of heated carbon dioxide The contents of the tank *n* are then distilled to recover the grease and the solvent The latter is returned to the reservoir *f*

The apparatus shown in fig 134 (Kissling-Bremen, *Leim und Gelatine*, p. 35) forms a good example of a continuous type of extractor. It consists of an extraction chamber E, into which the material can be introduced and removed after extraction through the manhole *b*. The solvent is distributed over the goods by means of fine sieves covered with linen placed underneath the manhole *b* and over the opening at the bottom of the extraction chamber. Beneath the lower sieve is a steam pipe by means of which the solvent may be expelled from the goods after extraction. K is a condenser which is connected to the extraction chamber by a delivery tube. The solvent which is driven out of the extracted goods is condensed and collected in the receiver R. From this the solvent passes through the pipe *s*, governed by means of a cock, back to the extracting chamber, filling it completely. From this it siphons into the distilling apparatus B, carrying with it the dissolved grease. As it siphons over it a fresh supply of solvent is drawn in from the container R. The dirty solvent in B is evaporated by means of the steam pipe shown, and the vapour passes through the condenser K, the condensed solvent being collected again in R. This container is provided with a separator at W and *r* for the removal of air, and water may be drawn off at *e*. The tubes *g* and *h* and valves *p* and *d* conduct the vapours of the solvent from the extractor E and the vessel B to the condenser at K. Through *y* the vapour of the solvent can be led from B to E, and the dissolved grease and solvent through *h* and *c* to the distiller B.

CHAPTER XXI.

WASHING MACHINES.

Washing.—The importance of washing has already been referred to. It can hardly be overestimated. Not only is washing of importance as a cleansing process, but it is relied upon to remove both the chemicals used in any process and their reaction products from the goods. Washing also prevents the danger of interaction between the chemicals used in two succeeding processes. No time spent in washing is ever wasted, and, however thoroughly a process has been carried out, it will be counteracted by incomplete washing. Thus, for example, if, after the lye boil, the residual lye and the dissolved impurities are not thoroughly removed by washing, an incomplete boil results. The first essential for washing, viz. a plentiful supply of pure water, has already been emphasised. The second is the use of a suitable machine.

Washing Machines.—The roller washing machine for treatment of cloth in the rope has already been generally described, and the arrangement of its parts is obvious from fig. 136 It is still perhaps the most generally used machine, and serves its purpose quite well, though rather extravagant in water. The cloth enters in duplicate ends by the pot-eyes at either side, and is threaded round the wince rollers in the box and the bottom bowl into a series of spirals separated by glazed pot or wooden pegs. The ends emerging together at the centre of the machine and driven by the rotation of the bowls are subjected to a series of nips and immersions in the liquor box or beck, whereby each part is respectively treated with fresh liquor and the dirt squeezed out. Just prior to the final nip, which is the severest by reason of the bowl being wrapped round in the centre with several layers of cloth, the cloth meets the water jet that supplies the machine, so that the incoming water meets the cloth at its cleanest stage. An additional roller is often mounted above the upper of the main pair to further dry the cloth and reduce dilution of the liquors subsequently applied.

The bowls are of beech or sycamore, 22 inches or 24 inches in diameter, the lower being the driver. The diameter of this determines the rate of output of the machine. Thus when it has been skimmed up several times (to take out irregularities which occur with wear), its reduced diameter lessens the output of the machine, and it must be finally utilised as a top bowl, whose diameter is of less importance, as pressure is effected by the weighted levers which bear on its end as well as by its own weight. To reduce grooving in the places where the spirals of cloth are nipped, the peg rail should be mounted with a traversing adjustment, and from day to day gradually moved across the interspaces between the successive threadings. As the operation of the machine demands sudden stoppages and variation of speed, especially during threading up, the driving-power should be applied through a friction clutch having a good margin of friction surface. This further enables the operator to set his clutch

for ordinary driving so that he can avoid excessive tension on lighter goods and prevent a "break-out" or rupture at the weakest point of the rope of

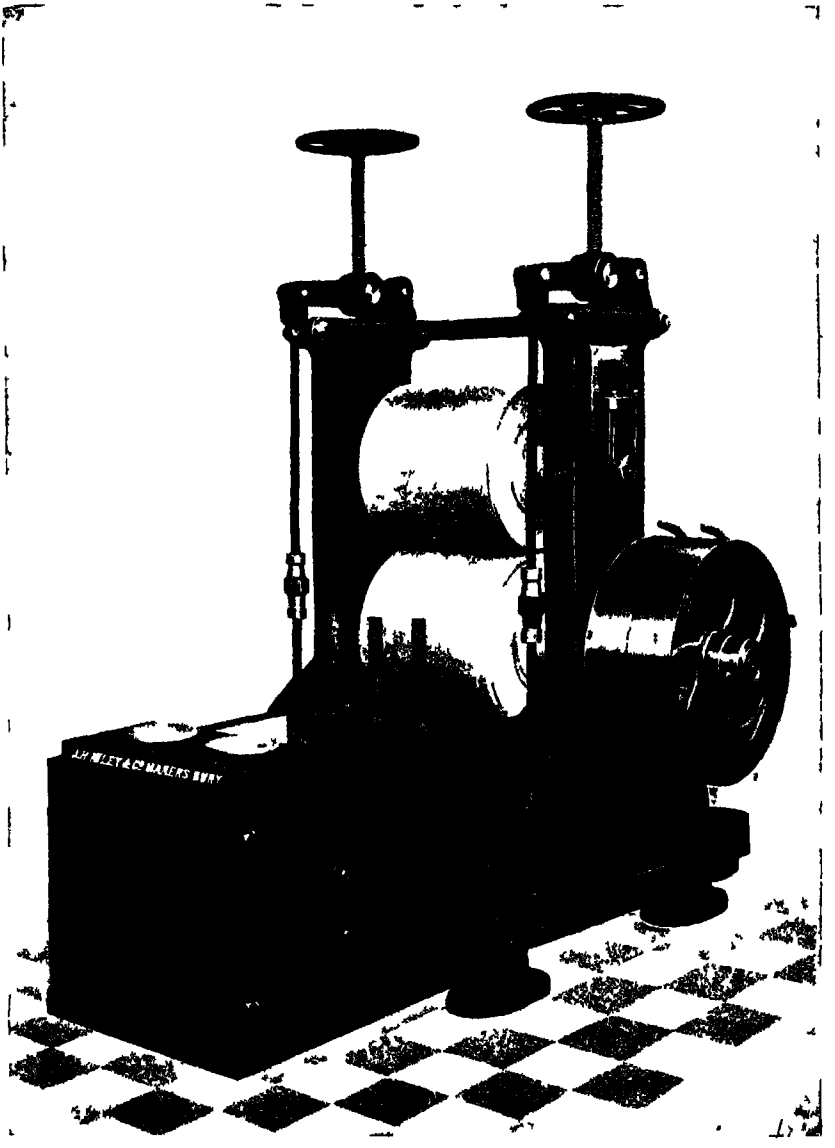


FIG. 135 – Squeezing machine.

cloth, when by reason of an entanglement or obstruction at a pot-eye a sudden strain is produced

It would probably be worth while to apply to the drive of all washing machines

an automatic stopping motion set to liberate the clutch whenever the tension exceeded a given amount, such limiting tension being readily adjustable

To avoid repetition of the labour involved in threading up the machine when once threaded with cloth, a length of linen tape is tied to the tail end of the cloth at the incoming end of the machine, and this is drawn through in the wake of the rope and used to guide the next one through the machine A precaution to be observed in using the machine is to have the bowls skimmed up in a lathe when they show signs of irregularity, otherwise the rollers nipping lightly in one place and allowing slip in others will subject the cloth to excessive local tension, friction, and pressure The jerking of the upper bowl which accompanies such irregularity tends to cut the cloth in falling If the diameter of the driving bowl gets too small the area of contact between cloth and bowl is reduced, and the loss of driving power may result in slipping and friction Any local defects in bowls, such as are caused by the accidental passage of some hard foreign substance carried in by the cloth, must be detected and quickly removed, and the bowl plugged with a wooden peg to restore the surface to the original diameter The damage that can be caused by the regular periodic marking or cutting of the cloth in this way demands that it should be frequently inspected after washing, so that the cause may be detected and removed The distance between such cuts sometimes serves as an index as to which machine is doing the damage, the detection being effected by reference to the girth of the bowls This kind of damage gives point to the necessity for keeping the machine boxes clean and carefully sieving before impregnation by lime, and frequent inspection of bowls and winces

Irregular washing and even mechanical damage may occur through uneven pressures being applied to the two ends of the bowl, and damage may also result, especially in the squeezing machine from a relative horizontal movement between the bowls, due to end play in the bearings Such damage takes the form of tiny pin holes in the cloth It is sometimes necessary during washing to pay particular attention to prevent the production of what is termed "water blown" cloth This means that if the nip be too severe, and the texture of the cloth or selvage such as to gather up more water than can be rapidly liberated from it, the strain accompanying the expulsion of the water tends to burst the threads The remedy is reduced pressure of nip or slower running

A squeezing machine (fig 135) is employed to give the final wash as the cloth leaves the croft It consists of a pair of narrow but heavy bowls, the lower of cotton and the upper of wood or wrapped with rope The pressure between the two bowls is effected by compound levers and weights The mangle is preferably fitted with a long, narrow trough containing a series of winces or rollers to extend the path of the cloth through the water Several of these may be fixed above the water level to facilitate the expulsion of water tangentially from the cloth The flow of clean water, as in all washing machines, enters at the end nearest to the delivery of the cloth and overflows at the other A steam pipe also enters at the delivery end to warm up the water for the final wash

Squeezing machines are also employed, in which the nip occurs between two metal rollers, one of which is grooved

In treating light delicate goods the ordinary roller washing machine would cause fraying, and in such cases the application of tension and squeezing must be reduced to a minimum A machine made by Messrs S Walker and Sons (fig 136) for this purpose is provided with the ordinary driving bowls, but the cloth is only nipped between them on entering and on leaving the machine The driving during the intermediate course through the machine is effected by threading

each turn over a pair of light adjustable swing jockey rollers, which cause it to bear against and pass under the lower bowl instead of through the nip. The cloth drops by its own weight from the delivery roller on to the washing-box, where it runs slack and is thence drawn up by the feed rollers through the guiding peg rail, beneath which are a pair of beaters to agitate the cloth and expel the

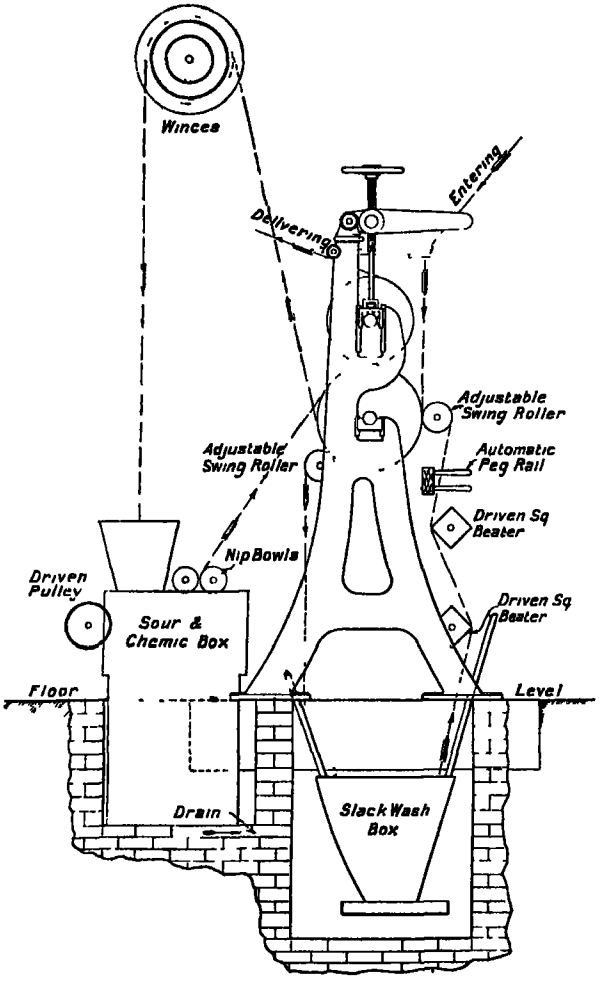


FIG 136.—Walker's non-tensional roller washing machine.

dirty water. The peg rail is mounted on a swivel and connected by a lever to the striking gear of the clutch in such manner that, if an entanglement between the slack coils in the box reaches the peg rail and is not unravelled by the beaters, the peg rail is swung round and stops the machine, instead of allowing a tear to occur.

The machine is, of course, equally applicable to chemicking and souring, and may be provided with an auxiliary impregnating machine, as shown in fig. 136.

The application of beaters to washing machines for heavy goods is seen in the Brideson (figs 137 and 138) and the Davis and Eckersley machine (fig 139), made by Messrs Jackson & Bro The former consists of a rectangular water box,

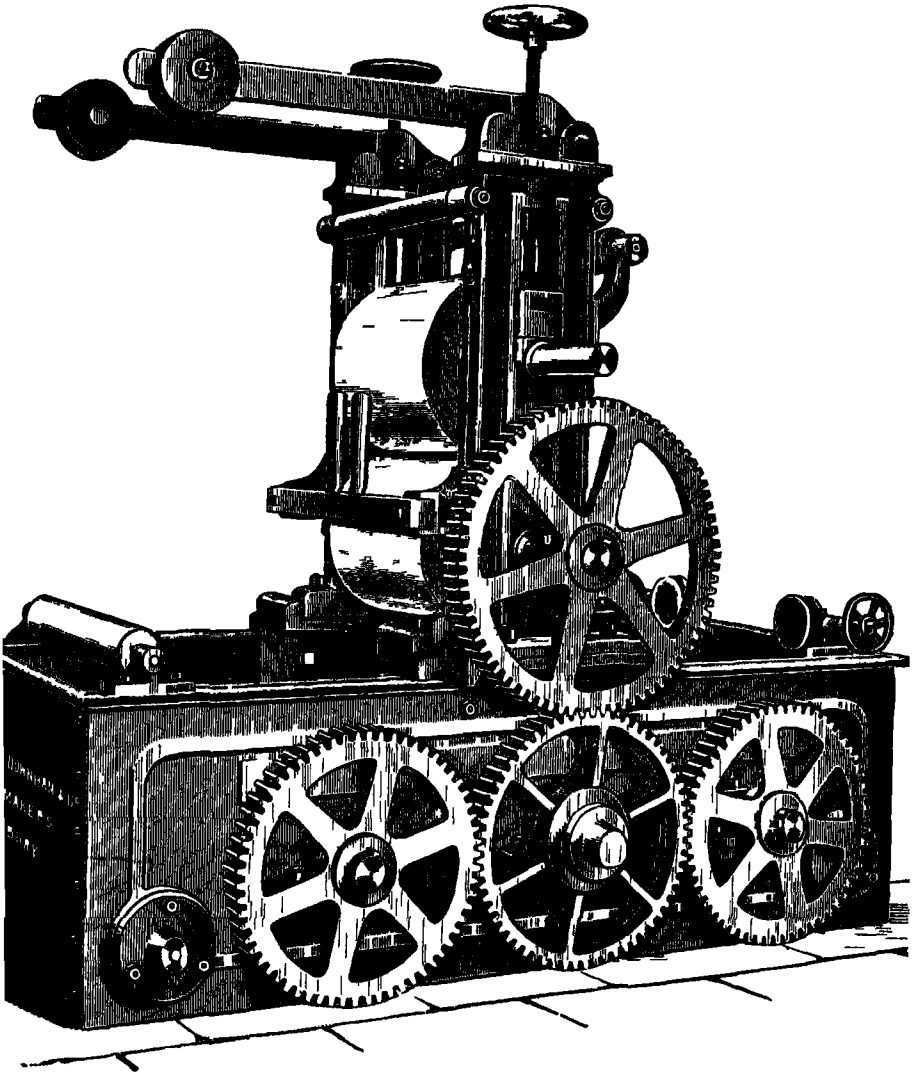


FIG. 137.—Washing machine with beaters

carrying at one of the upper horizontal corners a pair of pot eyes, and at each of the three others a guide roller Lying in the central horizontal plane of the box are two shafts and a flat board midway between them On each shaft is mounted a flat beater, or frame, carrying two horizontal bars of wood, parallel to, and equidistant from, the shaft When the latter is revolving these bars just miss the central board The shafts are geared together through an intermediate wheel,

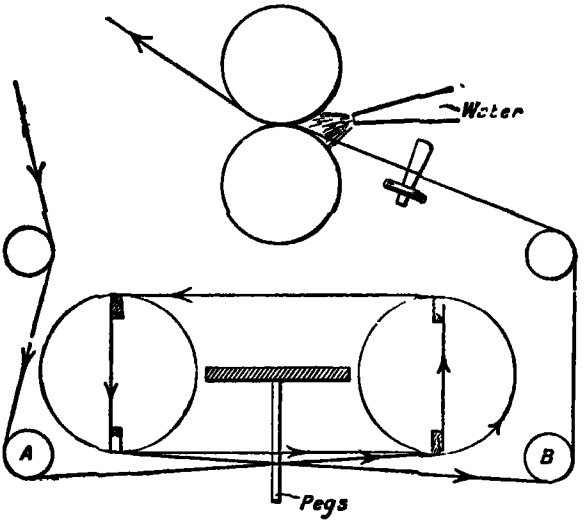


FIG 138.—Diagram of Brideson washing machine

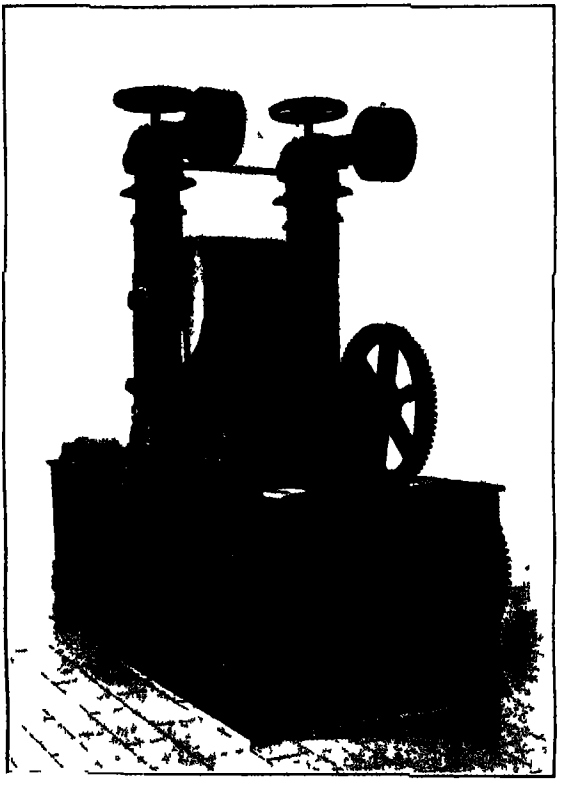


FIG 139.—Davis-Eckersley washing machine.

which is driven from the shaft of the lower of the two squeezer bowls, which are mounted above the box, with the usual cheeks, pressure levers, and a peg rail

Fig. 138 shows the method of threading up the Brideson machine. Cloth runs from wince A and thrice round the beaters (the folds being separated by vertical rods), thence to B, and then up to a nip between the squeeze bowls and out The beaters revolve at a high speed, and twice in each revolution—when the beaters are in the same horizontal plane as the central board—each lap of the cloth is banged against the boards, and to this effective agitation and beating of the cloth is due the excellent cleansing action of the machine But care is required in the regulation of the beaters to take up wear, or correct, by the adjustment of the wooden bars, any discrepancy between the tensions caused respectively by the beaters and rollers The mounting of the beater shaft in the box of the machine should be such that the whole beater and shaft can be lifted out of the box to repair the beater or unravel a tangle of cloth, if such should occur.

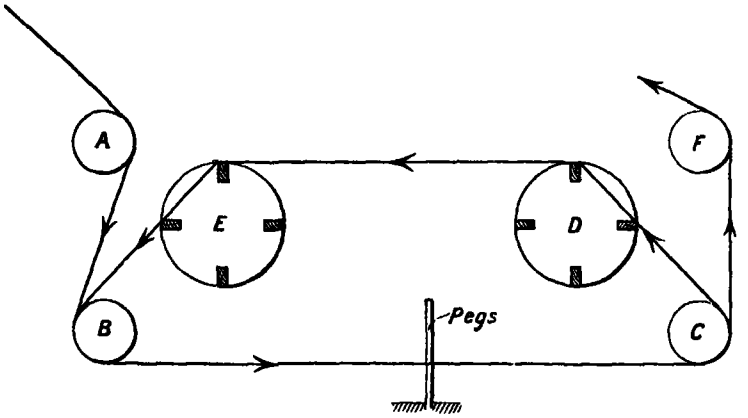


Fig 140.—Diagram of modified Brideson wash-box

The removal may be facilitated by the withdrawal of a slide above the pedestal, which leaves a vertical gap in the side of the box

The improvement on the above arrangement, known as the Davis and Eckersley's machine (fig 139), consists in replacing the squeezers by a miniature roller washing machine for three turns or spirals of cloth on each side The jet of clean feed water is supplied to this upper section of the machine (which contains the cleanest cloth), after which it flows into the lower (Brideson) section. In the latest machines the beaters are replaced by winces round which the cloth passes

The lower section of the machine is seen in fig. 140. The passage of the cloth is as follows, the letters referring to the parts indicated in the diagram: A, B, C, D, E, B, C, D, E, B, C, D, E, B, C, F. It is found that this washing effect is ample (especially in view of the extra treatment in the top section), and the rather excessive strains involved in the jerking and banging of the cloth, tending to crack the selvages, are thus avoided The action becomes one of a series of movements of the cloth alternately through the washing water and the air, the agitation in the latter case dashing out the dirty water

In discussing the above washing machines, it may be noted that no mention is made of the use of soap, which forms so important a part in the cleansing of

yarn and other cotton fabrics that lend themselves to the milling processes. The chief reason is that where soap is used as a detergent in the treatment of piece goods, it is employed in the kiers, and the extraction of the dirt-laden detergent effected first by rinsing the cloth with water while still in the kier, and subsequently in the washing machine The high speed of transmission of the cloth through the machine that can be conveniently applied to piece goods in the rope is the main reason for adopting this mode of cleansing

Milling.—The most effective of all mechanical operations for thoroughly intermingling a detergent or other liquid with cloth or yarn, and subsequently washing out the same, and such impurities as have become associated with it, is that of milling The operation is only applicable to small quantities of goods at one time; but it affords the means of treating small quantities very quickly and thoroughly. The chief machines in which the method is employed are the fulling stocks and dolly machine or "tom-tom," and their chief application is to lace, hosiery, and yarn.

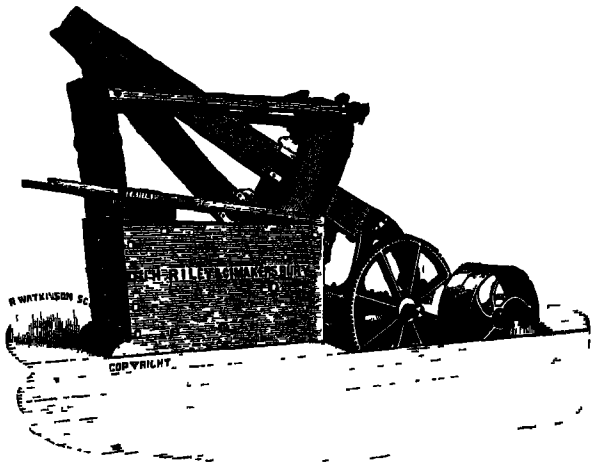


FIG 141 – Soaping and fulling stocks

The stocks (fig 141) consist of a wooden chamber made to receive a milling arm, shaped in a circular arc of about 5 feet external radius, centred vertically above the closed end of the chamber, and about which centre the arm is made to oscillate by means of a tappet arrangement The latter consists of a wheel carrying several tappet blocks, which engage with an extension from the swinging arm lifting the latter, and then releasing it to swing with its own weight on to the fabric in the chamber These swinging arms may be made in duplicate, and by their alternate descent and the shapes of the striking face and of the closed end of the chamber, a series of revolving motions is imparted to the fabric which cause it to present a continually changing surface to the impact of the milling arm The fabric is impregnated with a hot soap solution, and this is thoroughly worked into it to emulsify the dirt A drain outlet is then opened and a spray of clean soft water turned on, the milling being continued till the soap is thoroughly extracted. A pair of such stocks is mounted one on either side of a soap-mixing box, fed by a water pipe and steam-heating coil. This may be divided into two sections, in one of which is mixed coarse soap for a first wash, and a finer soap solution tinted with blue to give a finishing effect. The

cleansing and whitening effect of soaping yarn in the stocks after it has passed through the boiling and bleaching process is most striking.

A very similar effect is produced in the dollying machine (fig 142), which

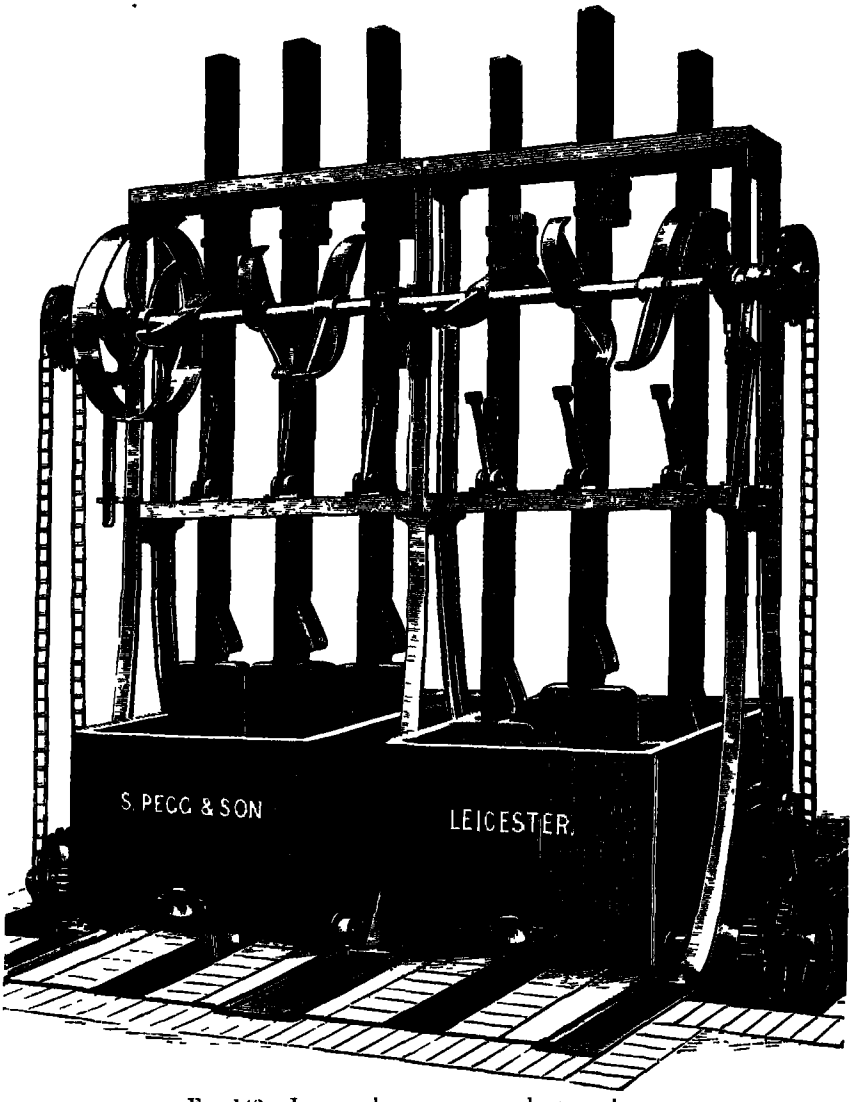


Fig 142.—Improved scouring or washing machine

admits of a greater bulk of material being simultaneously treated, and lends itself particularly to the treatment of very dirty lace goods which could not be satisfactorily cleansed in the roller washing machine and are therefore treated throughout in bundle form instead of the rope The milling action is not so severe as that of the stocks, but is distributed more evenly to all parts of the

material. It consists of an oak tub, about 3 feet deep and 6 feet in diameter, revolving about its vertical axis by means of horizontal spur gearing, or, as in fig. 142, of a rectangular box made to travel backwards and forwards The tub is provided with a perforated false bottom covering a shallow well, with several outlets which can be opened or closed while the tub is revolving These feed into a circular trough and thence to the drain or to a well for recovery of the dirty suds The milling effect is produced by a row of beaters or fallers analogous to those of a beetling machine, and capable of vertical movement, being fitted by the engagement of their tappets with cams mounted on a shaft at the back of the machine The downward fall is produced by the weight of the beaters, but limited by a guide rail from quite reaching the bottom of the tub The stroke can be further adjusted by altering the height at which the tappets are fixed The cams are keyed to the shaft at different angles to distribute the load and impact on the fabric during the revolution of the shaft, and the striking face of the beaters or fallers is splayed out and the edges rounded so as to distribute the milling effect The beaters may be put out of action by the hinged detents shown, or by inserting a peg through a hole in their shank when at the top of their stroke, the hole being bored at a point just above the lower guide rail upon which the peg therefore rests and supports the beater The degree of milling is regulated by the number of beaters in action, their weight, and the extent of their stroke

The tub is surmounted by spray pipes for hot and cold water and tanks containing fresh and recovered soap solutions The bundles of lace, etc, are placed in the tub, which is then set revolving and fed with water and soap The beaters are then put into operation on one or both sides, and the degree of treatment is gauged by the number of 'turns,' *i e* revolutions or traverse motions of the tub

Other Washing Machines. — Before leaving the subject of washing machinery, mention may be made of machines applied to the washing of yarns, warps, chains, cops, silver, waste and raw cotton, etc Small articles in isolated pieces are sometimes washed in the dash wheel This is a cylindrical drum divided into compartments provided with access doors and central spray pipe and peripheral perforations for exit of the water (fig 143) During revolution the goods tumble about in their compartments, pressing on each other, and, being alternately soaked and drained, receive a uniform wash without excessive mechanical strain

Yarn in the chain formation, and warps in the rope or chain, may be washed in the machine similar to the rope washing and squeezing machines, but in this case the upper bowl is sometimes omitted, and the lower bowl replaced by a square beater to give additional agitation to the material Various machines have been devised for rinsing yarn in the hank, the main principles of which are a combination of dipping, reeling, and squeezing, by means of a set of rollers, carrying a few hanks each, and effecting a progressive motion through a stream of water towards the clean water supply at the delivery end The simplest machine, used in conjunction with the stocks, is the reeling machine, in which three or more square or hexagonal reeling drums surmount a rinsing box (fig 144) The hanks are opened out and slung over the reels, which revolve alternately in opposite directions The yarn following this motion is swilled through the water. The drums can be fed in rotation at a considerable rate by one attendant, and an adequate rinsing effect obtained to remove anything left in the yarn from the stocks A cheap type of machine serving its purpose fairly well consists of a series of reeling drums surmounted by squeeze rollers and spray pipes, radiating from, and revolving about, a common centre, over a circular rinsing

trough. A separate reeling motion is imparted to each drum This can be maintained irrespectively of the revolution of the system about the vertical centre,

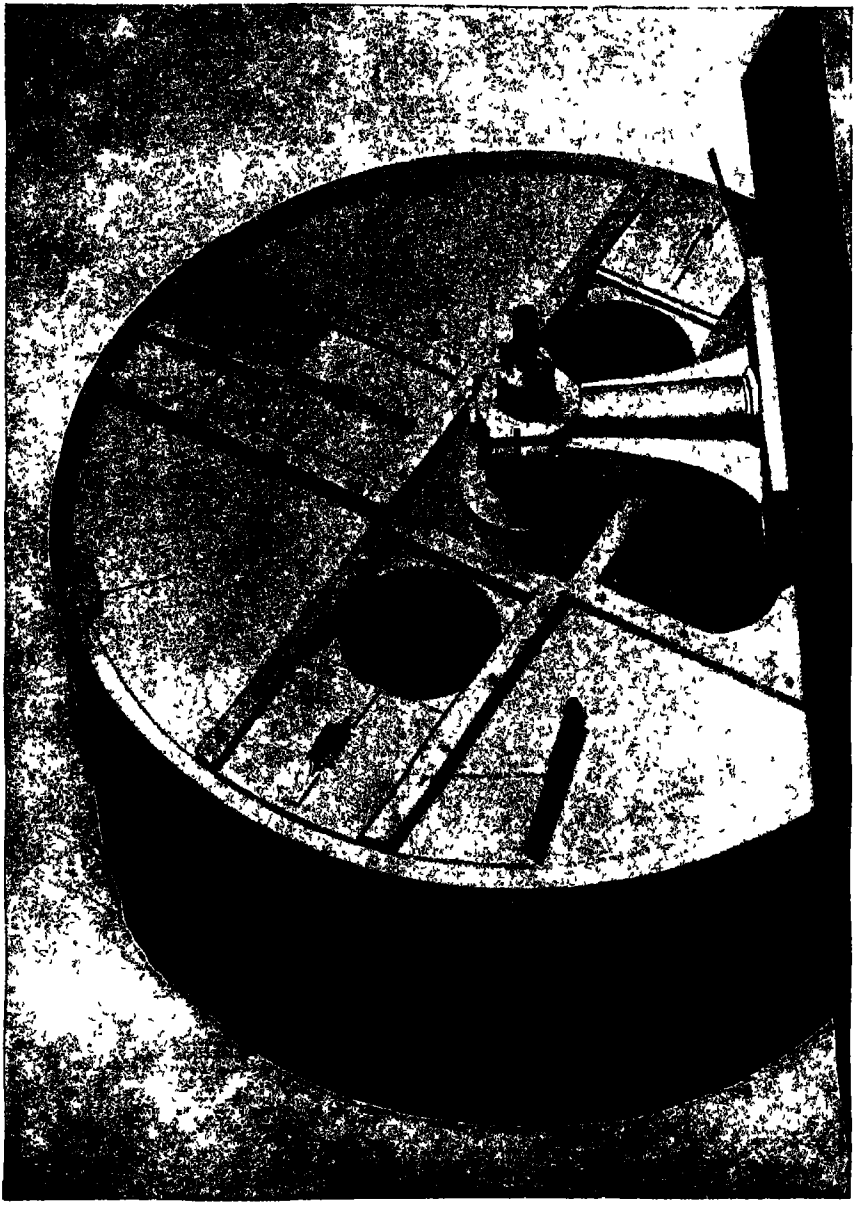


Fig. 143.—Dash wheel.

which motion can be arrested, and any individual drum emptied and filled. The clean water is only admitted to the sprays towards the end of the revolution,

and the drainage is circulated by a pump to spray the yarn in the earlier stages of its revolution

Other machines imitate the effect of rinsing by hand, which consists in grasping the hank and drawing it sharply backwards and forwards through the water

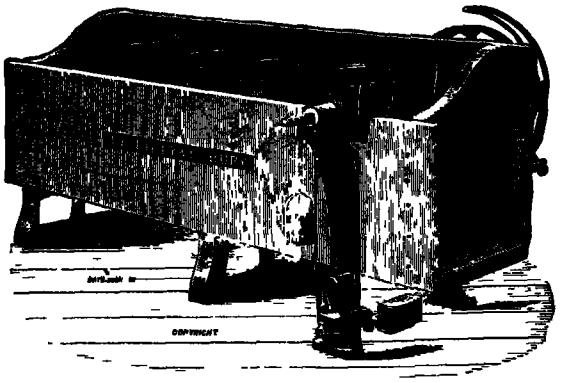


Fig 144 Hank washing and wringing machine

with a sweep of the wrist and elbow, meanwhile rotating the hank by varying the point at which it is grasped

A hank washing machine by Messrs John M Collins & Son, of Glasgow, illustrated in figs 145 and 146, is an example of the motions described in relation

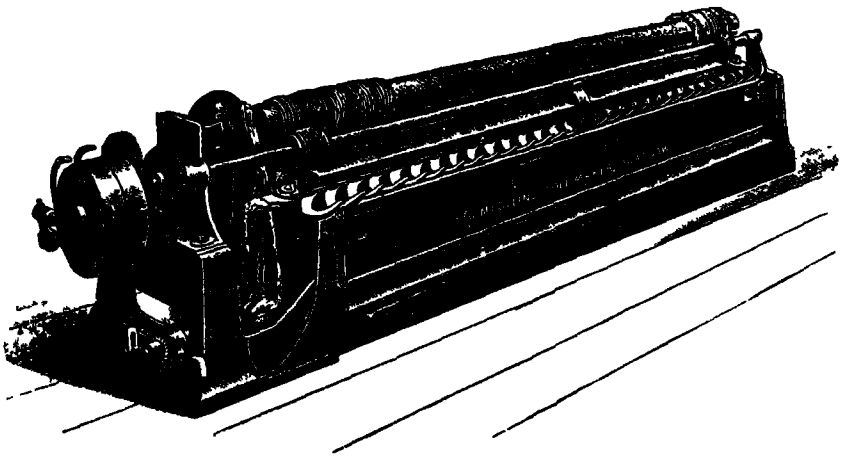


Fig 145 - Hank washing machine

to a slack (cloth) washing machine, but adapted to suit the manipulation of a closed loop or hank of yarn

The essential modifications lie in the suppression of axial projections, such as shafts or bearings on the top bowl or "pressing roller," so that hanks may be threaded thereon, and, after traversing the length of the washing machine, be removed from the roller at the delivery end

The pressing roller is supported and driven only by the peripheral contact between itself and the carrying roller and bearing pulleys, the latter occurring at opposite ends of the roller and the former throughout its length

At the two ends the rollers are somewhat tapered to graduate the initial and final nip, and at the delivery end is a rubber wheel to take the end thrust of the roller and assist in quitting the yarn

The hanks are guided along the roller by means of a series of brass hooks which travel in the form of an endless chain

The action of the machine is as follows —

The hanks are fed by hand, one at a time, around the feeding end of the pressing roller, and enter the nip between this and the carrying roller, revolving in the direction shown and dipping into the water box

The rinsing and squeezing then proceed as in an ordinary roller washing machine, until the guiding hooks deliver the hanks for removal by hand at the opposite end, and the operation is thus continuous

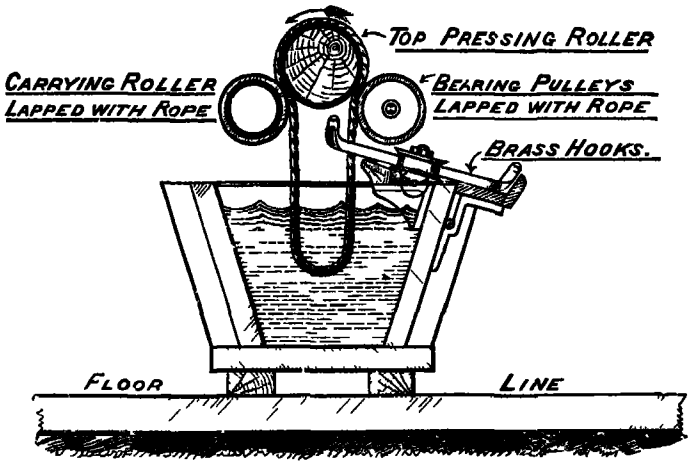


Fig 146 Cross section of hank washing machine

The rinsing effect may be augmented by the addition of a spray of water bearing on the top roller

The washing of raw cotton is effected in raking machines of the McNaughton type The loose material is fed by a brattise into a series of cisterns through which water is circulated vertically It is kept in motion by a series of rakes attached to a lever These sweep forward while engaging the material, then, rising above the level of the water, swing back to the beginning of the stroke, and, dipping into the liquor again, repeat the forward stroke Another series of mechanically operated rakes deliver the material from one division of the machine to the next, and finally propel it through a pair of squeezing rollers into a revolving breaker, to open it out

Where delicacy of handling is of secondary importance to that of thorough washing, machines based on the principle of the beating engine, as used for treatment of paper pulp, are employed These consist of an oval receiver, in which the material is circulated by means of a paddle The removal of dirty water is effected by means of a perforated drum which revolves in the stream of liquor, admitting the latter, but not the material, to its interior It is gathered

up in revolving buckets which drain their contents through a central tube or hollow shaft, above the level of the liquor in the race.

Another method of separating the liquor is by means of a stationary riddle

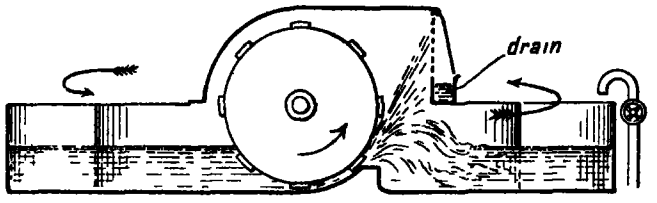


FIG 147.—Waste washing machine

or perforated sheet (fig 147) The liquor is dashed up against this by the paddle The angle at which the liquor is tangentially projected from the paddles is increased by curving the bottom of the race in which the paddle revolves, or inserting thereon a wedge-shaped block.

CHAPTER XXII

BLEACHING AGENTS, SULPHUR DIOXIDE AND ITS DERIVATIVES.

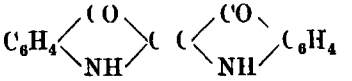
Much of the colouring matter of textile fabrics is associated with the impurities, and is removed simultaneously with these during the preliminary scouring processes. There are, however, residual colouring matters which cannot be removed in this way, but are capable of being decomposed into soluble simpler compounds or into colourless (or leuco) compounds by the action of oxidising or reducing agents. The reagents used for this purpose are termed 'bleaching agents." They are, as indicated, of two kinds—

1. Reducing bleaching agents
2. Oxidising bleaching agents

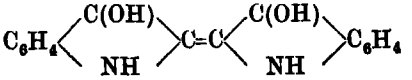
The reducing bleaching agents act, as a rule, by decomposing water, combining with the oxygen and liberating the hydrogen. Thus, with sulphur dioxide, sulphuric acid and hydrogen are produced—

$$SO_2+2H_2O=H_2SO_4+H_2$$

This hydrogen, being in the nascent state, is very active. When it acts upon colouring matters, it may either decompose them into simpler colourless compounds, or combine with them, forming addition products, termed leuco compounds. When leuco compounds are produced, they are often insoluble in water and cannot, therefore, be washed away, but remain on the fabric. Leuco-compounds are, in many cases, reoxidised to the original colouring matter when exposed to the action of air or an oxidising agent. This is determined by the chemical constitution of the colouring matter. This point may be illustrated by reference to the coal tar dyestuffs. Indigo has the formula



When it is treated with a reducing agent two atoms of hydrogen are absorbed and a leuco-compound, indigo white, is produced—



When indigo white is exposed to air, these two atoms of hydrogen are oxidised to one molecule of water, and the original indigo is reproduced. But, in some cases, the colouring matter is decomposed into two or more simpler compounds, or into a colourless compound which cannot be oxidised to the original colouring

matter If a dyestuff be an azo-compound (*i e* contains the group (—N=N—), it is split up into two amines by nascent hydrogen Thus

$$R—N\ N—R'+2H_2=R\ NH_2+R'NH_2$$

Or, again, if a dyestuff be a nitro-compound it is changed to an amine by nascent hydrogen—

$$RNO_2+3H_2=RNH_2+2H_2O$$

But in neither of these cases is the colouring matter reproduced by oxidation The natural colouring matters of textile fibres are not generally decomposed by nascent hydrogen, but form addition- or leuco-compounds which are gradually oxidised to the colouring matter on exposure to air Hence, the white which is produced by reducing bleaching agents is not permanent Wool, for example, which has been bleached by means of sulphur dioxide becomes gradually yellow on exposure to air

The chief reducing bleaching agents are—

1 Sulphur dioxide
2 Sulphurous acid and sulphites
3 Hydrosulphites

The Oxidising Bleaching Agents. These act either by decomposing water with the liberation of oxygen, or by giving up some of the oxygen which they contain Thus, chlorine liberates oxygen from water, while hydrogen peroxide splits up readily into water and oxygen—

$$2Cl_2+2H_2O=4HCl+O_2,$$
$$2H_2O_2=2H_2O+O_2$$

When the colouring matters of textile fabrics are oxidised they do not form addition compounds, but are broken up into simpler soluble substances which can be washed away with water Hence, the white which they produce is generally permanent

The more important oxidising bleaching agents are—

1 Chlorine
2 *Hypochlorous acid and hypochlorites*
3 Hydrogen peroxide and some metallic peroxides
4 Permanganates of sodium or potassium
5 Persulphates, perborates, percarbonates, persilicates, and perphosphates
6 Ozone and oxygen

The choice of a bleaching agent is governed by the nature of the fibre to be treated, the degree of bleaching required and the cost of the process

Sulphur Dioxide. -This body is produced when sulphur is burnt in air, or oxygen, traces of sulphur trioxide being simultaneously formed It may be prepared, also, by roasting iron pyrites, FeS_2, as in the manufacture of sulphuric acid (p 331) Sulphur dioxide is formed when a sulphite is treated with hydrochloric or sulphuric acid, or when certain heavy metals, such as copper, are dissolved in hot concentrated sulphuric acid—

$$Na_2SO_3+2HCl=2NaCl+H_2O+SO_2,$$
$$Cu+2H_2SO_4=CuSO_4+2H_2O+SO_2$$

Sulphur dioxide is a colourless gas, with the characteristic smell of burning sulphur It is heavier than air and can be collected by downward displacement

It is liquefied, under ordinary atmospheric pressure, at a temperature of −10° C The liquefied gas boils at −8° C and freezes at −76° C

Sulphur dioxide is very soluble in water, combining with it to form sulphurous acid, H_2SO_3—

$$SO_2+H_2O=H_2SO_3$$

This solution has an acid reaction and taste, and, when saturated with a base, such as sodium hydroxide, gives salts termed sulphites If a solution of sulphurous acid in water be boiled, the sulphur dioxide is all expelled That is, the acid is unstable and cannot be prepared by simply concentrating its aqueous solution, but, when a saturated solution is frozen, crystals are deposited, having the composition $H_2SO_3\ 8H_2O$ An aqueous solution of sulphur dioxide changes gradually into sulphuric acid, hydrogen being also formed—

$$SO_2+2H_2O=H_2SO_4+H_2$$

This reaction, as mentioned above, is the basis of its bleaching action. Sulphur dioxide is a powerful and useful reducing agent Thus, it changes chlorine into hydrochloric acid in the presence of water—

$$Cl_2+2H_2O+SO_2=2HCl+H_2SO_4$$

Other examples of its reducing action are—

1 It reduces iodic acid, HIO_3, to iodine—

$$2HIO_3+4H_2O+5SO_2=5H_2SO_4+I_2$$

2 Arsenic pentoxide is reduced to trioxide—

$$2As_2O_5+4SO_2+4H_2O=As_4O_6+4H_2SO_4.$$

3 Potassium permanganate is decomposed into manganese sulphate and potassium sulphate—

$$2KMnO_4+3H_2SO_4+2H_2O+5SO_2=K_2SO_4+2MnSO_4+5H_2SO_4$$

The reduction of potassium permanganate is more readily understood if it be remembered that it can give up a portion of its oxygen in presence of an oxidisible compound, such as sulphur dioxide This oxidises the sulphur dioxide to trioxide, which in presence of water becomes changed into sulphuric acid, thus

$$\begin{aligned}&(1)\ 2K_2MnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O\\&(2)\ 5O+5SO_2=5SO_3\\&(3)\ 5SO_3+5H_2O=5H_2SO_4\end{aligned}$$

4 If sulphur dioxide be passed into a solution of ferric sulphate, the ferric salt is reduced to ferrous sulphate—

$$Fe_2(SO_4)_3+SO_2+2H_2O=2FeSO_4+2H_2SO_4.$$

5 Chromates, or bichronates, in the presence of sulphuric acid, are similarly reduced by sulphur dioxide to chromic salts—

$$\begin{aligned}&(1)\ K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O.\\&(2)\ 3O+3SO_2+3H_2O=3H_2SO_4\end{aligned}$$

It should be noted that a reducing agent does either one of two things, viz.—

1. Removes oxygen from another compound.
2. Decreases the proportion of the non-metallic constituent.

Thus, the change from $FeCl_3$ to $FeCl_2$ is a reduction, as is, also, that from Fe_2O_3 to FeO.

Some of the reducing actions of sulphur dioxide are important in textile operations. It can be used as an "antichlor" to remove traces of chlorine from bleached goods. In bleaching with potassium permanganate, it is used to reduce and dissolve the oxides of manganese, which are precipitated on the goods—

$$Mn_2O_3+SO_2+H_2O+H_2SO_4=2MnSO_4+2H_2O.$$

Under certain circumstances, sulphur dioxide can act as an oxidising agent. Thus, if magnesium ribbon be ignited and plunged into a jar of the gas, it continues to burn, and combines with the liberated oxygen, magnesium sulphide being also formed

The Sulphites.—Since sulphurous acid is dibasic, two series of salts, acid and normal, exist. Thus, in the case of sodium there are—

1. Sodium bisulphite (acid sulphite), $NaHSO_3$
2. Sodium sulphite (normal sulphite), Na_2SO_3.

The sulphites of sodium and potassium are readily soluble in water, those of other metals, such as calcium, only sparingly soluble.

The bisulphites of sodium and calcium are made by passing sulphur dioxide, obtained by burning sulphur, into sodium hydroxide solution or milk of lime—

$$NaOH+SO_2=NaHSO_3$$

The normal sulphites are prepared by neutralising the hydroxide with sulphurous acid—

$$2NaOH+H_2SO_3=Na_2SO_3+2H_2O.$$

Sodium bisulphite, $NaHSO_3$, is a colourless substance, readily soluble in water Its solution acts as though it were a mixture of sulphurous acid and sodium sulphite—

$$2NaHSO_3=Na_2SO_3+H_2SO_3$$

When treated with a mineral acid, it is decomposed with the liberation of sulphur dioxide—

$$NaHSO_3+HCl=NaCl+H_2O+SO_2$$

When sodium bisulphite, or its aqueous solution, is exposed to air, it becomes oxidised to sodium bisulphate—

$$NaHSO_3+O=NaHSO_4$$

Sodium bisulphite is acid to phenolphthalein but neutral to methyl orange

Sodium metabisulphite, $Na_2O(SO_2)_2$ or $Na_2S_2O_5$, is a useful reducing agent, since it is comparatively stable It is a solid substance, soluble in water and containing 67·4 per cent. of available sulphur dioxide. When dissolved in water it gives up some of its sulphur dioxide, and the whole of it can be liberated by sulphuric acid—

$$Na_2O(SO_2)_2+H_2SO_4=Na_2SO_4+H_2O+2SO_2.$$

Normal sodium sulphite, $Na_2SO_3\,10H_2O$, is a colourless crystalline substance readily soluble in water Its aqueous solution is alkaline to both phenolphthalein and methyl orange. It is readily oxidised to sodium sulphate when exposed to air or the action of oxidising agents It is decomposed when heated, giving a mixture of sodium sulphate and sodium sulphide—

$$4Na_2SO_3=3Na_2SO_4+Na_2S.$$

Sulphur dioxide may be obtained from a sulphite, as mentioned above, by treating it with a stronger acid. When a solution of sodium sulphite is boiled with finely divided sulphur, the latter is dissolved and sodium thiosulphate is formed—

$$Na_2SO_3+S=Na_2S_2O_3.$$

Hydrosulphites.—When an aqueous solution of sulphur dioxide is treated with zinc dust the zinc salt of hydrosulphurous acid, $H_2S_2O_4$, is formed—

$$2H_2SO_3+Zn=ZnS_2O_4+2H_2O.$$

The action is probably one of reduction. Mellor (*Modern Inorganic Chemistry*, p 426) gives the following explanation :—

$$(1)\ Zn+H_2SO_3 = ZnSO_3+H_2.$$
$$(2)\ 2H_2SO_3+2H=H_2S_2O_4+2H_2O.$$
$$(3)\ H_2S_2O_4+Zn = ZnS_2O_4+H_2$$

If a solution of sodium bisulphite containing dissolved sulphur dioxide be used the reaction is

$$2NaHSO_3+SO_2+Zn=Na_2S_2O_4+ZnSO_3+H_2O.$$

If the zinc be precipitated by means of milk of lime and the mixture filtered, a solution of sodium hydrosulphite is obtained, from which the crystalline salt $Na_2S_2O_4\ 2H_2O$ may be separated Sodium hydrosulphite is a colourless soluble substance from which hydrosulphurous acid may be liberated by treatment with acetic acid. But hydrosulphurous acid is unstable, and decomposes gradually into a mixture of sulphuric and sulphurous acid and sulphur Sodium hydrosulphite is a powerful reducing agent, either in aqueous, acid, or alkaline solutions. It acts, probably, by decomposing water forming sodium hydrogen sulphate and liberating nascent hydrogen—

$$Na_2S_2O_4+4H_2O=2NaHSO_4+3H_2$$

Although it is not of great importance as a bleaching agent, sodium hydrosulphite is used extensively in dyeing as a stripping agent and for reducing indigo to indigo white

Hydrosulphites give stable addition-compounds with formaldehyde, which are also important as stripping agents for dyestuffs Thus, hydrosulphite N.F. is a double compound of the composition $Na_2S_2O_4\ 2HCHO$ When sodium hydrosulphite is dissolved in 40 per cent formaldehyde solution (formalin) and cooled, crystals of formaldehyde bisulphite, $NaHSO_3\ CH_2O\ 2H_2O$, and formaldehyde hydrosulphite, $NaHSO_2\ CH_2O\ 2H_2O$, are produced This may indicate that commercial sodium hydrosulphite is a mixture of bisulphite and hydrosulphite combined with one molecule of water.

$$NaHSO_3+NaHSO_2+H_2O=Na_2S_2O_4.2H_2O$$

If this be so, hydrosulphurous acid must be H_2SO_2 and not $H_2S_2O_4$ as generally represented, and when treated with formaldehyde the following reaction takes place —

$$Na_2S_2O_4\ 2H_2O+2CH_2O+2H_2O=NaHSO_3CH_2O\ H_2O+NaHSO_2CH_2O\ 2H_2O$$

The formaldehyde compounds of hydrosulphites are comparatively stable in aqueous solutions. When treated with dilute acetic acid, hydrosulphurous acid is liberated slowly at ordinary temperatures, the reaction only being completed

at the boiling-point. A similar decomposition is brought about by the action of steam These compounds are sold under such names as decrolein, formosul, etc.

Bochter (Brit. Pat. 182776) uses sodium hydrosulphite for bleaching cotton in the following manner · The goods are treated with caustic soda lye (preferably in a vacuum at a temperature below 100° C) containing from 0·05 to 0·1 per cent. of sodium hydrosulphite After heating for four hours at 50° to 70° C , the goods are washed, soured and bleached with a solution of a hypochlorite.

The Use of Reducing Bleaching Agents.—Sulphur dioxide and its derivatives have only a very limited use in the bleaching of cotton. They are, however, employed largely for animal fibres, such as wool and silk, which cannot be bleached with chlorine or bleaching powder without risk of causing structural damage. Unions containing wool and silk are frequently bleached by means of sulphur dioxide, but unless the operation is carried out with great care and every trace of sulphurous acid removed subsequently, tendering commonly results. Sulphur dioxide bleaching is generally termed "stoving." Sulphur is burnt in a stove and the resulting sulphur dioxide is led into a chamber in which the goods are hung on wooden frames. Sometimes the sulphur is simply placed in pots and burnt in the chamber itself This method is not to be recommended since, if there is deficiency of air, some of the sulphur may be sublimed and condense on the goods causing stains No metal which is attacked by acid must be used in the construction of the chamber, and iron in particular must be absent The goods should be damp, though not sufficiently wet to allow of the sulphurous acid collecting in the lower portions. When the chamber is filled with the sulphur dioxide it is closed and the goods are left in it for some hours. From 5 to 7 lbs of sulphur are necessary for every 100 of material to be bleached. When the bleaching is complete, the excess of sulphur dioxide is blown out and the goods are removed and washed thoroughly with water In the case of unions, the wool adsorbs sulphur dioxide and it is very difficult to remove it by washing with water alone Hence, after washing away as much of it as possible with water, the bleached goods are worked in a bath of dilute sodium carbonate solution and then washed again with water The sodium sulphite which is formed is much more readily removed than the sulphurous acid Sulphur dioxide may be removed also by placing the goods in water and adding a solution of potassium permanganate in small quantities as long as it is decolorised. This treatment is followed, as before, by a bath of sodium carbonate and washing with water It should be noted that union goods containing vegetable fibres are often tendered through small quantities of acid which have been retained by the wool

Liquid sulphur dioxide is used, occasionally, as a source of the gas, but, for some rather obscure reason, it does not bleach as well as sulphur dioxide produced by burning sulphur It is possible that the difference may be due to the fact that the latter contains traces of sulphur trioxide

Sodium bisulphite is used in an aqueous solution containing from 10 to 15 lbs. for every 100 material Since only half of its sulphur dioxide is available in aqueous solution, the bath is either acidified or the goods, after soaking in the bisulphite solution, are put into a bath of acid to complete the bleaching action. In this case the bisulphite is used as a standing bath. The reactions are—

$$(1)\ 2NaHSO_3 = Na_2SO_3 + H_2SO_3.$$
$$(2)\ Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2SO_3.$$

If normal sodium sulphite be employed the bath is acidified at the beginning in accordance with the equation (2).

The Analysis of Sulphurous Acid and Sulphites.—Sulphur dioxide in solution is estimated by titration with decinormal iodine solution Iodine is reduced in the same way as chlorine in accordance with the equation

$$I_2+2H_2O+SO_2=2HI+H_2SO_4$$

From 1 to 5 grammes of the sample, according to its strength, are weighed in a stoppered weighing bottle, washed into a 500 c c. flask, and diluted to the mark with recently boiled distilled water (*i e* free from oxygen).

A suitable volume (25 c c.) is withdrawn by means of a pipette and run into a stoppered bottle which contains a known volume of decinormal iodine solution, which must be sufficient to oxidise all the sulphur dioxide and still leave an excess of iodine. After rotating the bottle gently, the excess of iodine is titrated with decinormal sodium thiosulphate solution This is run in from a burette, replacing the stopper and mixing the contents of the bottle after each addition. When the colour of the iodine has been nearly discharged a drop of starch solution is added. A blue colour, due to iodide of starch, is produced. The thiosulphate solution is now added carefully till this blue colour just disappears This will happen as soon as all the iodine has been changed by the sodium thiosulphate into sodium tetrathionate—

$$2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6.$$

Each cubic centimetre of decinormal iodine which has disappeared corresponds to 0 0032 gramme of sulphur dioxide This method is applicable to either sulphurous acid, bisulphites, or sulphites

The titration may be made, also, by adding the sulphurous acid solution from a burette to a measured volume of decinormal iodine solution, till the colour of the iodine disappears If the sulphurous acid be added slowly with constant stirring, good results are obtained. In the case of sulphites dilute hydrochloric acid must be mixed with the iodine solution

Iodine solution cannot be run into sulphurous acid unless excess is used as described above. The oxidation of the sulphurous acid is not complete under these circumstances and inaccurate results are obtained. According to Treadwell, this is caused by the fact that the hydriodic acid reduces part of the sulphurous acid to sulphur—

$$SO_2+4HI=2I_2+2H_2O+S$$

Solutions of sulphurous acid may be titrated also with decinormal or normal alkali Either phenolphthalein or methyl orange may be used as indicators The production of a pink colour with phenolphthalein corresponds to the equation

$$H_2SO_3+2NaOH=Na_2SO_3+2H_2O,$$

since sodium bisulphite is acid towards this indicator

Sulphurous acid is acid to methyl orange, but sodium bisulphite is neutral. Hence, if this indicator be used, the end point corresponds to the equation

$$H_2SO_3+NaOH=NaHSO_3+H_2O.$$

Mixtures of sulphites and bisulphites or of bisulphites and free sulphurous acid can be titrated also.

Mixtures of Sulphurous Acid and Sodium Bisulphite.—A measured volume of the solution is titrated with standard sodium hydroxide, methyl orange being used as the indicator till the solution is just neutral, *i.e.* till the free sulphurous acid is all changed to sodium bisulphite. The volume of sodium-hydroxide

solution used is read off. A drop of phenolphthalein solution is then added and the addition of the sodium hydroxide continued till a faint pink colour appears. This indicates that the whole of the sodium bisulphite has been changed into normal sulphite. The amount of free sulphurous acid is calculated from the first reading, while the second gives the total sulphur dioxide (factor 0·0032) present as bisulphite If the sulphur dioxide present as free sulphurous acid be deducted from the total, the difference gives that present as bisulphite in the original solution In the analysis of mixtures of bisulphite and normal sulphite the acid sulphite is first titrated with standard sodium hydroxide and phenolphthalein. Methyl orange is then added, and the total SO_2 present as bisulphite is found by titration with standard hydrochloric acid.

It is necessary, sometimes, to identify or estimate small quantities of sulphurous acid in fabric or other materials The best way is to distil the material with steam, condensing the distillate by means of a vertical condenser, the end of which dips beneath the surface of some bromine water. The excess of bromine is removed by adding a few drops of hydrochloric acid to the distillate and boiling it Barium chloride sodium is then added and, after further boiling, any precipitated barium sulphate is filtered off and weighed

When sodium bisulphite is titrated with sodium hydroxide, phenolphthalein being used as indicator, no distinction is made between bisulphite and bisulphate Thus:

$$NaHSO_3+NaOH=Na_2SO_3+H_2O,$$
$$NaHSO_4+NaOH=Na_2SO_4+H_2O$$

Further, titration with iodine does not differentiate bisulphite and bisulphate

The following method (*J Leather Trades Chemists*, 1922, p 199) may be used with advantage Two grammes of the bisulphite are dissolved in water and titrated with normal sodium hydroxide solution for total acidity (a), phenolphthalein being used as indicator If, now, 10 c c of neutralised formalin be added, sodium hydroxide will be liberated in accordance with the equation

$$Na_2SO_3+HCHO+H_2O=NaHSO_3.HCHO+NaOH$$

This liberated sodium hydroxide is then titrated with normal hydrochloric acid (b). Then,

1 If $a=b$, the impurities present are only neutral salts

2 If $a>b$, acid impurities are present, and the difference, $a-b$, is calculated into sodium bisulphate.

3. If $b>a$, normal sulphite is present and the difference, $b-a$, is calculated into Na_2SO_3.

An interesting paper on the composition and evaluation of commercial sodium bisulphite by Harrison and Carroll (*J S C I*, 1925, p 127T) may be included

Commercial sodium bisulphite is invariably sold on the basis of its sulphur dioxide content The chief factors determining its deterioration are its physical structure and the presence of air and moisture. The authors have investigated the principle of oxidising bisulphite to bisulphate by means of hydrogen peroxide and titrating the acidity by means of standard sodium by dioxide solution. They find that the end point is quite sharp and recommend the following method of analysis.—

Total Sulphur Dioxide.—About 0·25 gramme of the sample is weighed out on a watch glass and the whole dropped gently into a large beaker containing 50 c.c. of N/10 iodine solution in 500 c.c. of distilled water. The whole is then

stirred until the bisulphite has dissolved completely, when the unabsorbed iodine is titrated with N/10 thiosulphate solution.

Sulphur Dioxide existing as Metabisulphite.—Exactly 10 c c of hydrogen peroxide solution (20 vols) are added to each of three flasks containing 50 c c. of distilled water and 0·5 c.c. of methyl orange indicator solution (0·2 per cent.) If this solution is acid in reaction this should be adjusted by the careful addition of N/5 sodium hydroxide solution until only a faint red tint is visible About 1 gramme of the sample is weighed out quickly and transferred to the flask with the addition of a few cubic centimetres of water. This operation is repeated with a second flask The flasks are then shaken and cooled if necessary About 50 c c of distilled water are now added to the flask representing the blank experiment, so that the concentration of the indicator is approximately the same in all three flasks at the end of the titrations to be performed. The contents of the two flasks containing bisulphite are then titrated with N/5 sodium hydroxide solution until the tints of the indicator in all three flasks are identical. Proceeding in this way it will be found that the sulphur dioxide values obtained in duplicate do not differ by more than 0·2 per cent

Sodium sulphate is determined by observing the precautions of Giles and Shearer, to which reference has been made already.

The following results were obtained by the authors from the analyses of five samples of commercial bisulphite —

Sample	A	B	C	D	E
	Per cent	Per cent	Per cent	Per cent	Per cent
Total SO_2	65 78	65 45	64 95	57 83	63 40
SO_2 existing as metabisulphite	64 15	63 62	62 54	53 05	60 42

From these were calculated the amounts of metabisulphite, $Na_2S_2O_5$, contained in these samples, also the percentages of the normal sulphite, Na_2SO_3, present on the assumption that the difference between the total SO_2 and that existing as $Na_2S_2O_5$ is a measure of the quantity of normal sulphite A determination of the amounts of sulphate contained completed the analyses, giving the following values —

	A	B	C.	D	E.
	Per cent	Per cent	Per cent	Per cent	Per cent.
Sodium metabisulphite, $Na_2S_2O_5$.	95 23	94 45	92 86	78 76	89 69
Sodium sulphite, Na_2SO_3 .	3 21	3 60	4 75	9 41	5 87
„ sulphate, Na_2SO_4	1 61	1 91	2 41	9 82	4 12
	100 05	99 96	100 02	97 99	99 68

Samples A, B, and C were crystalline powders and, as the above analyses show, contained little or no moisture. Independent tests showed that the water content of these was less than 0·1 per cent. Sample D was an amorphous powder and contained about 2 per cent of moisture; subsequent analyses of this sample proved it to be unstable, oxidation taking place at a fairly rapid rate. Sample

E was a fine powder and contained a small percentage of moisture. It was fairly stable, but the metabisulphite content was low. Examination of these samples for thiosulphate and salts of other sulphur acids gave negative results.

Considering the results of these analyses, and also the appearance of the samples physically, it would appear that the stability of commercial sodium bisulphite is a function of its crystalline structure and also of its lack of moisture content It is evident, further, that the assumption that commercial bisulphite contains sodium hydrogen sulphite is incompatible with the results of analysis; for if the latter salt were a constituent of the commercial material, the tabulated results as given above would appear thus ·

	A	B	C.	D.	E.
	Per cent.	Per cent	Per cent.	Per cent	Per cent
Sodium hydrogen sulphate .	104 35	103 50	101 74	86 30	98 27
,, sulphite .	3 21	3 60	4 75	9 41	5 87
,, sulphate	1 61	1 91	2 41	9 82	4 12
	109 17	109 01	108 90	105 53	108 26

The Analysis of Sodium Hydrosulphite.—Hydrosulphites are oxidised to sulphites by alkaline solutions of chromates, but the sulphites thus formed are not oxidised further—

$$2Na_2CrO_4+3Na_2S_2O_4+2NaOH=6Na_2SO_3+Cr_2O_3+H_2O.$$

Knecht (*J.S.C.I.*, 1915, p 421) based the following process on these facts. From 0 1 to 0·2 gramme of the hydrosulphite is added to 20 c c of decinormal potassium bichromate solution made alkaline with sodium hydroxide. The solution is boiled for three or four minutes The oxide of chromium is then filtered off and boiled with water and sodium peroxide till it is dissolved, and the excess of hydrogen peroxide expelled. The chromium present as chromate is then determined by titration and the corresponding hydrosulphite is calculated

Merriman (*J.S.C.I.*, 1923, p 291) gives a method depending upon the fact that when sodium hydrosulphite is treated with excess of formaldehyde, it breaks up into a mixture of sodium sulphoxylate formaldehyde ($NaHSO_2.CH_2O\ 2H_2O$) and sodium bisulphite formaldehyde ($NaHSO_3.CH_2O.H_2O$), according to the equation

$$Na_2S_2O_4+2CH_2O+4H_2O=NaHSO_2.CH_2O\ 2H_2O+NaHSO_3\ CH_2O.H_2O.$$

Sodium bisulphite formaldehyde is not acted upon by iodine in neutral or acid solutions. Sodium sulphoxylate formaldehyde reacts with iodine in neutral or acid solution, according to the equation

$$NaHSO_2\ CH_2O.2H_2O+4I=NaHSO_4+CH_2O+4HI.$$

Thus the action of iodine on a solution of sodium hydrosulphite, in the presence of excess of formaldehyde, is

$$Na_2S_2O_4+2CH_2O+4I+3H_2O=NaHSO_4+4HI+CH_2O+NaHSO_3.CH_2O.$$

That is, one molecular weight of $Na_2S_2O_4$ reacts with four atoms of iodine. Hence, 1 c.c. N/10 iodine solution is equivalent to 0·004352 gramme of sodium hydrosulphite, $Na_2S_2O_4$.

The method of application is as follows: After sampling, 10 grammes are weighed. A litre flask is used, cut off at the neck to within 1 inch of the mark, and provided with a well-fitting rubber stopper. From 20 to 40 c c. of formaldehyde are placed in the flask and distilled water is added, leaving room for another 50 c.c. After mixing the water and formaldehyde, the weighed hydrosulphite is introduced through a dry funnel with a short wide stem. The funnel is washed down rapidly, the volume made up to the mark, the stopper inserted, and the contents well mixed About 100 c.c. of water, followed by 20 c.c. of the hydrosulphite solution, are placed in a beaker and 50 c c. of decinormal iodine solution are at once added. The light brown liquor is left for two minutes and the excess of iodine is then back-titrated with decinormal thiosulphate solution

A somewhat similar process is described by Messrs Brotherton & Co. (*J.S.C.I.*, 1923, p 1131), in which a mixture of potassium iodide and iodate is used instead of iodine solution.

CHAPTER XXIII.

CHLORINE AND ITS DERIVATIVES.

Chlorine—Hypochlorous Acid, Bleaching Powder, and their Use in Bleaching.

Chlorine belongs to the group of elements known as the halogens The family includes the following elements —

Fluorine	atomic weight,	19 06
Chlorine	,,	35 50
Bromine . . .	,,	79 76
Iodine	,,	126 54

From member to member in this family a gradual and well-marked alteration of chemical and physical properties can be traced Thus fluorine is a colourless and chlorine a heavy yellow gas Bromine is a liquid and iodide a crystalline solid The halogens all combine with hydrogen, giving acids containing one atom of the halogen and one of hydrogen. Fluorine reacts with hydrogen with explosive violence, even in the dark, chlorine readily in sunlight, bromine only slowly, and iodine only when heated The increase in atomic weight is thus accompanied by a weaker affinity for hydrogen The power of combining with oxygen varies in the opposite way Fluorine refuses to combine at all, the oxides of chlorine are unstable, while iodine pentoxide, I_2O_5, is a very stable compound The relative decrease of chemical affinity with increase of atomic weight is also well shown by the fact that chlorine will replace both bromine and iodine in its compounds, while bromine replaces iodine, but not chlorine Fluorine is able to replace even chlorine

Chlorine is never found free in nature. Its commonest compound is sodium chloride or common salt, but magnesium, potassium, calcium, and silver chlorides are also common

Chlorine is obtained very easily from salt by heating it with manganese dioxide and dilute sulphuric acid The reaction takes place in accordance with the equations

(1) $2NaCl+H_2SO_4=Na_2SO_4+2HCl$
(2) $MnO_2+H_2SO_4=MnSO_4+H_2O+O$
(3) $2HCl+O \quad =H_2O+Cl_2$

Or, adding these together, we have

$$2NaCl+MnO_2+2H_2SO_4=Na_2SO_4+MnSO_4+2H_2O+Cl_2.$$

The manufacture of chlorine commercially is intimately connected with the Leblanc soda process, the first stage of which consists in treating salt with sulphuric acid, whereby hydrochloric acid and sodium sulphate are produced.

Chlorine is also produced when hydrochloric acid is heated with oxidising agents other than manganese dioxide, such as potassium bichromate—

$$K_2Cr_2O_7+14HCl=2KCl+2CrCl_3+7H_2O+3Cl_2$$

On the large scale chlorine is made chiefly by (*a*) the Deacon process, and (*b*) the electrolysis of solutions of sodium chloride. In the Deacon process, hydrochloric acid gas mixed with air is passed over balls of pumice, saturated with a solution of cuprous chloride Cu_2Cl_2, heated to a temperature a little below 400° C. The cuprous chloride plays the part of a catalytic agent or oxygen carrier remaining unchanged at the end of the operation—

$$2HCl+O+Cu_2Cl_2=Cu_2Cl_2+H_2O+Cl_2.$$

It is probable that the reaction takes place in stages, thus

$$Cu_2Cl_2+2HCl+O=2CuCl_2+H_2O,$$
$$2CuCl_2=Cu_2Cl_2+Cl_2$$

Or, it may be that an oxychloride of copper is first formed, thus .

$$2Cu_2Cl_2+O_2=2Cu_2OCl_2,$$

which breaks down into cupric chloride, thus

$$Cu_2OCl_2+2HCl=2CuCl_2+H_2O.$$

The chlorine produced in this manner contains water-vapour, free hydrochloric acid, and excess of air The hydrochloric acid is removed by washing the gas with water, but the air remains. The chlorine made by this process is suitable for the manufacture of bleaching powder.

The electrolytic process consists of passing an electric current through a solution of salt in a double cell. This method is combined with the preparation of sodium hydroxide (p. 351) When a solution of sodium chloride is electrolysed it is resolved into its ions Na and Cl The chlorine is liberated at the anode and the sodium at the kathode This sodium at once decomposes water, forming sodium hydroxide—

$$Na+H_2O=NaOH+H.$$

If the electrodes are close together, the chlorine dissolves in the solution of sodium hydroxide formed, and sodium hypochlorite results But if the electrodes are separated by a porous diaphragm this reaction does not take place, and both chlorine and sodium hydroxide can be obtained separately.

Properties of Chlorine.—Chlorine is a yellowish-green gas, possessing a very pungent smell When inhaled, it attacks the mucous membrane of the nose and throat, and, if taken in large quantities, is a dangerous poison. Chlorine is 35·5 times heavier than hydrogen and 2·45 times heavier than air. It may be collected, therefore, by downward displacement The gas is easily liquefied by cooling it to −34° C Liquid chlorine has a yellow colour It freezes to a solid at −102° C It is stored in cast-iron or steel cylinders. It is used in the extraction of gold from its ores, and may be employed in the preparation of bleaching liquors (p 452).

Chlorine is very soluble in water. The solubility at different temperatures is given in the following table :—

Temperature.	Litres of Chlorine dissolved by 1 Litre of Water.
0° C.	3 430
8° C.	3 040
10° C	3 000
17° C	2 370
50° C	1 490
100° C.	0 150

When a saturated solution of chlorine in water is frozen, crystals of chlorine octahydrate, $Cl_2 8H_2O$, are formed A solution of chlorine in water (chlorine water) has a yellow colour and the characteristic smell of chlorine When kept, particularly if exposed to light, hydrochloric acid is formed gradually, in accordance with the equation

$$Cl_2+H_2O=2HCl+O$$

Very dilute solutions of chlorine in water contain hypochlorous acid—

$$H_2O+Cl_2 \rightleftharpoons HCl+HOCl$$

This reaction, as indicated, is reversible Moist chlorine is a powerful oxidising agent, owing to its power of decomposing water with the liberation of nascent oxygen A piece of damp litmus paper is bleached instantly when placed in a jar of chlorine Among other oxidising actions is the formation of sulphuric from sulphurous acid—

$$Cl_2+H_2O+H_2SO_3=2HCl+H_2SO_4$$

Another oxidation of a different type is the changing of ferrous chloride in the ferric salt—

$$FeCl_2+Cl=FeCl_3$$

The bleaching action of chlorine is due, primarily, to its great affinity for hydrogen This property is illustrated in many ways When chlorine and hydrogen are mixed in equal volumes and exposed to a strong light, or if an electric spark be passed through the mixture, they combine to form hydrochloric acid with explosive violence This, however, does not take place if both gases are absolutely dry But 1 part of water in 300 millions of the mixture is sufficient to promote the reaction If a jet of burning hydrogen be lowered into a jar of chlorine, the hydrogen continues to burn with the formation of hydrochloric acid

If sulphuretted hydrogen be mixed with chlorine, it is decomposed, hydrochloric acid and sulphur being formed—

$$H_2S+Cl_2=2HCl+S$$

Chlorine decomposes ammonia, producing hydrochloric acid and nitrogen The liberated nitrogen combines with more chlorine to form nitrogen chloride, which is a very powerful explosive Organic compounds, such as proteins, which contain amino groups, are converted into chloramines when treated with chlorine (p 50)

Or again, a piece of filter-paper, moistened with turpentine, $C_{10}H_{16}$, and placed in an atmosphere of chlorine, bursts into flame owing to the heat produced by the action between the chlorine and hydrogen, the carbon being liberated at the same time—

$$C_{10}H_{16}+8Cl_2=16HCl+10C$$

Nearly all hydrocarbons react with chlorine, forming either addition or substitution compounds, according to whether they are unsaturated or saturated Thus, ethylene, C_2H_4, forms ethylene chloride, $C_2H_4Cl_2$, while in the case of methane, which is saturated, the hydrogen atoms can be replaced successively, giving ultimately carbon tetrachloride CCl_4

Chlorine combines, also, directly with many other elements both non-metallic and metallic, giving compounds termed chlorides Phosphorus burns in an atmosphere of chlorine, forming phosphorus pentachloride, PCl_5

Among the metals, sodium, potassium, iron, aluminium, and mercury all unite readily with gaseous chlorine to form chlorides. The metallic chlorides can be obtained, also, by the usual methods, such as the action of hydrochloric acid upon the metal or its oxide.

In some cases, the chlorides are only very slightly soluble in water, and can be prepared by precipitation. Thus, silver chloride, mercurous chloride, and lead chloride are thrown down when hydrochloric acid or a soluble chloride is added to a solution containing a soluble salt of the metal.

As a rule, the metallic chlorides are soluble in water, but, besides those already mentioned, cuprous and aurous chloride are only sparingly soluble. Lead chloride, $PbCl_2$, dissolves in boiling water, but crystallises when the solution is cooled. Some of the chlorides, although soluble, are hydrolysed by water Aqueous solutions of the chlorides of magnesium, zinc, or aluminium are acid to litmus-paper, and when evaporated leave a residue of oxychloride (or basic chloride), hydrochloric acid being driven off—

$$MgCl_2+H_2O=MgOHCl+HCl$$

Bismuth chloride is completely precipitated as a basic salt when its solution in hydrochloric acid is diluted largely with water—

$$BiCl_3+2H_2O=Bi(OH)_2Cl+2HCl.$$

Stannic chloride, $SnCl_4$, is a fuming, colourless liquid which boils at 113·9° C It unites with water, giving a series of crystalline hydrates, $SnCl_4\ 3H_2O$, $SnCl_4\ 5H_2O$, and $SnCl_4.8H_2O$. Aqueous solutions of stannic chloride are hydrolysed gradually, yielding stannic hydroxide—

$$SnCl_4+4H_2O=Sn(OH)_4+4HCl.$$

Many of the chlorides unite with others, forming double salts Thus, carnallite is a double chloride of potassium and magnesium, $KCl\ MgCl_2.6H_2O$ Magnesium ammonium chloride, $MgCl_2\ NH_4Cl\ 6H_2O$, is prepared by mixing solutions of the constituent chlorides and allowing the mixture to crystallise. This compound is soluble in ammonium hydroxide. If, therefore, ammonium chloride be present in a solution containing magnesium chloride, the metallic hydroxide is not thrown down when ammonia is added

Chlorine gas has, hitherto, not been used much as a bleaching agent, owing partly to the difficulty attending its manufacture in small quantities and the transport of liquid chlorine. But liquid chlorine is now comparatively easy to handle and is suitable for many purposes, which will be described later

Bromine, a heavy red liquid, boiling at 59° C and freezing at −70° C, is prepared in a similar manner to chlorine Its chemical affinities are, as we have seen, less strong than those of chlorine, and it is sometimes used for bleaching silk goods. With caustic soda, bromine gives compounds similar to those of chlorine.

Nitro-hydrochloric acid, or aqua regia, is a powerful bleaching agent. Although not used for cotton goods, it is sometimes employed for silk Aqua regia is prepared by mixing nitric and hydrochloric acids in the proportions represented by the equation

$$3HCl+HNO_3=2H_2O+NOCl+Cl_2.$$

The chlorine, being in the nascent condition, has very powerful bleaching properties, acting, of course, by decomposing water with the liberation of nascent oxygen. The mixture is diluted with water and heated to a temperature of

40° to 60° C for use The goods after bleaching must be thoroughly washed till quite free from acid, after which they are sometimes subjected to the action of a bath of sulphurous acid and again washed Great care must be taken not to use a strong bath To obtain a good effect the process may be repeated till the required degree of whiteness is obtained

Compounds of Chlorine with Hydrogen and Oxygen.—Chlorine combines with hydrogen and oxygen in several proportions, giving rise to the following acids —

$HClO$, hypochlorous acid.
$HClO_2$, chlorous acid
$HClO_3$, chloric acid
$HClO_4$, perchloric acid.

The first two of these are unstable, and exist only in aqueous solution These acids may be regarded as the hydrates of a series of oxides They are—

Cl_2O, chlorine monoxide
ClO_2, chlorine peroxide
Cl_2O_5, chlorine pentoxide.
Cl_2O_7, chlorine heptoxide

Their combination with water may be represented by the following equations —

$$Cl_2O+H_2O=2HClO,$$
$$2ClO_2+H_2O=HClO_2+HClO_3,$$
$$Cl_2O_5+H_2O=2HClO_3,$$
$$Cl_2O_7+H_2O=2HClO_4$$

Hypochlorous Acid, HOCl.—This acid may be prepared by dissolving chlorine monoxide in water The oxide, which is a yellow gas, is made by passing chlorine over dry, freshly precipitated mercuric oxide in a cooled tube The chlorine monoxide is then led into a receiver cooled in a mixture of ice and salt It condenses to a yellowish brown coloured liquid which boils at 5° C at a pressure of 738 mm It is very unstable, and explodes, when heated, forming a mixture of chlorine and oxygen It dissolves readily in water, giving hypochlorous acid

Dilute solutions of hypochlorous acid, together with hydrochloric acid, are obtained when chlorine is passed into water The reaction is a reversible one, represented by the equation

$$Cl_2+H_2O \rightleftharpoons HCl+HOCl$$

The direction in which this reaction proceeds is governed largely by the hydrochloric acid When the quantity is small the reaction proceeds from left to right, forming hypochlorous and hydrochloric acids, until a state of equilibrium is reached As soon as the hydrochloric acid is increased beyond this point, either by direct addition or by increasing the quantity of chlorine, the reaction tends to be reversed, and the hypochlorous acid is decomposed as quickly as it is produced In the presence of large excess of hydrochloric acid hypochlorous acid cannot exist at all

According to Ornstein (*J Soc Dyers and Col*, 1921, p 255), at atmospheric temperature the reaction takes place from left to right if not more than 0 1 gramme of chlorine per litre is present, while at higher temperatures the quantity of chlorine producing the same degree of hydrolysis is greater He claims that,

in this way, solutions of hypochlorous acid can be prepared which are free from chlorine or hypochlorites.

It is clear, from the equation given above, that if the hydrochloric acid be removed as quickly as it is produced, much more concentrated solutions of hypochlorous acid could be obtained from the action of chlorine on water. Now, while hydrochloric is a strong acid, hypochlorous acid is a very weak one, being unable to decompose even carbonates Hence, if powdered calcium carbonate be suspended in the water the hydrochloric acid will be neutralised, while the hypochlorous acid remains in the solution—

$$2HCl+CaCO_3=CaCl_2+H_2CO_3.$$

Freshly prepared mercuric oxide, or sodium carbonate or bicarbonate, may be substituted for calcium carbonate The reactions are—

$$2HgO+2Cl_2+H_2O\rightleftharpoons HgO.HgCl_2+2HOCl,$$
$$CaCO_3+2Cl_2+H_2O\rightleftharpoons CaCl_2+2HOCl+CO_2,$$
$$Na_2CO_3+\ Cl_2+H_2O\rightleftharpoons NaHCO_3+HOCl+NaCl.$$

But all these reactions are reversible. When the concentration of hypochlorous

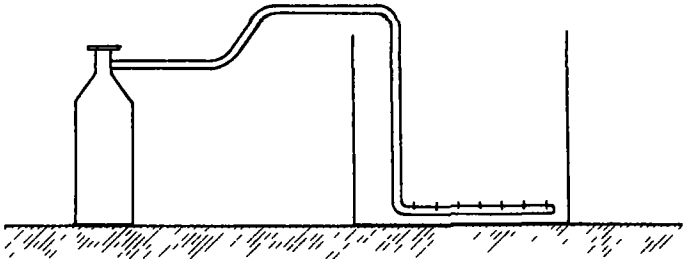


Fig 148.—Chlorine apparatus

acid exceeds a certain point, free chlorine is always present in the solution That is, only comparatively dilute solutions can be prepared in this manner

Ornstein has patented the use, for bleaching, of dilute solutions of hypochlorous acid prepared in this way The bleaching liquor may be made by introducing the chlorine into a bath of water containing the goods which it is desired to bleach. It must be observed that Ornstein's patent does not claim the method of preparing hypochlorous acid by passing chlorine into water containing suspended chalk, etc. This is a matter of common knowledge. It claims the use of such dilute solutions as are obtainable by the direct action of chlorine on water.

When preparing large quantities of hypochlorous acid solution, a cylinder of liquid chlorine may be used. The water and calcium carbonate must be placed in a vat lined with cement, and the delivery tube for the chlorine, made of lead, should pass to the bottom of the vat and be perforated with small holes. Solution of the chlorine should be assisted by gentle movement of the liquor. Fig 148 shows a suitable form of apparatus.

In another patent method (Eng. Pat 122888, 2nd May 1918) the water or other liquid to be saturated is supplied to the inner chamber of an atomiser arranged near the top of a receiving tank, and the supply of chlorine gas is connected with the outer chamber of the atomiser. The main supply of both chlorine and water is governed by interconnected valves, so that one cannot be opened without the

other. A perforated globular chamber of earthenware is fitted over the delivery orifice of the atomiser, to spread the mixture of liquid and gas. The tank is provided with a siphon discharge pipe and a vent flue, connected with the upper part of the tank by means of a siphon, to prevent excess of pressure.

Claim is also made in U.S Pat, 1261572, 2nd April, 1918, for a method of decomposing water at 100° C. with chlorine Steam and chlorine are made to react with one another at this temperature, and the aqueous hydrochloric acid is removed, by condensation, the more volatile hypochlorous acid being then absorbed by caustic alkali

Taylor and Bostock prepare hypochlorous acid by distilling a mixture of bleaching powder with thirty times its weight of water and twice its weight of boric acid According to these authors (*Bleaching Powder and its Action in Bleaching*, p 37), as long as about thirty times its weight of water is maintained a practically pure solution of hypochlorous acid is obtained. If, however, much less water be used more chlorine is produced If 10 grammes of bleaching powder are distilled with 300 c c of water and any amount of boric acid from 15 to 20 grammes, the first 50 or 100 c c. distilled off may be regarded as practically pure hypochlorous acid, giving only a slight immediate turbidity with silver-nitrate solution (*i.e.* indicating the presence of hydrochloric acid) The solution of hydrochlorous acid so prepared is usually from 1·5 to 2N/10, and contains from 4 to 5 grammes of pure hypochlorous acid per litre

Other weak acids give a similar result, if the amount used be only a little more than is necessary to neutralise the free lime present in the bleaching powder Acetic and phosphoric acids were both used by Taylor and Bostock in this way Carbon dioxide, also, decomposes a solution of bleaching powder, but the products depend upon the temperature of the reaction Taylor and Bostock state that when carbon dioxide is bubbled through a mixture of bleaching powder and water, at low temperatures, only chlorine is evolved, but as the temperature is raised hypochlorous acid begins to be produced The proportion of hypochlorous acid to chlorine increases gradually with the temperature, till at the boiling-point practically pure hypochlorous acid is obtained

A solution of hypochlorous acid may be prepared from a dilute solution of bleaching powder by adding just enough dilute hydrochloric acid to neutralise both the free calcium hydroxide and the calcium hypochlorite. Thus

$$Ca(OH)_2+2HCl=CaCl_2+2H_2O,$$
$$Ca(OCl)_2+2HCl=CaCl_2+2HOCl$$

The pH value of hypochlorous acid is about 6·0, while bleaching-powder solution is strongly alkaline. If dilute hydrochloric acid be stirred in till the mixture has a pH value of about 6, when tested by a suitable indicator, the solution contains very little chlorine But the slightest excess of hydrochloric acid causes the decomposition of hypochlorous acid—

$$HOCl+HCl=H_2O+Cl_2$$

Properties of Hypochlorous Acid.—Pure hypochlorous acid cannot be prepared, nor can dilute solutions be concentrated, nor distilled, without decomposition with the production of hydrochloric acid and free chlorine Hypochlorous acid, prepared by the method of Taylor and Bostock, even when the distillation is carried out under reduced pressure, contains always some free hydrochloric acid and traces of chlorine produced thus

$$HOCl=HCl+O,$$
$$HOCl+HCl=H_2O+Cl_2.$$

If excess of hydrochloric acid be added to hypochlorous acid the whole of the chlorine is immediately liberated.

It is stated often that solutions containing 5 per cent. of hypochlorous acid can be prepared by concentration of dilute solutions, and that such solutions have a yellow colour and a characteristic smell

The solution of Taylor and Bostock contains about 5 grammes per litre Though colourless, it, also, has this so-called characteristic smell But if shaken with calcium carbonate the smell disappears, indicating that it is due to chlorine. Moreover, the original distillate has a pH value corresponding to that of hydrochloric acid, while, as stated above, the hydrogen-ion concentration of hypochlorous acid is much less. Dilute aqueous solutions of hypochlorous acid are colourless and devoid of smell. When kept in the dark at a low temperature they are moderately stable, but if exposed to light, or when warmed, they decompose rapidly, both oxygen and chlorine being formed in accordance with the equations given above

According to Taylor (*J. Soc Dyers and Col*, 1922, p 93) the decomposition probably takes place in two stages, chloric acid being a product of the reaction—

$$(1)\ 3HOCl \rightleftharpoons HClO_3 + 2HCl$$
$$(2)\ 2HCl + 2HOCl = 2H_2O + 2Cl_2.$$

Taylor found that when a solution of silver nitrate is mixed with hypochlorous acid, at first only a slight milkiness and a white precipitate of silver chloride is formed The decomposition of the hypochlorous acid proceeds rapidly under these conditions, that is, the removal of the hydrochloric acid as soon as it is produced. This suggests the reversibility of the equation

$$3HOCl \rightleftharpoons HClO_3 + 2HCl.$$

Hypochlorous acid is soluble in certain organic solvents, such as ether, chloroform, and carbon tetrachloride, especially if a little alcohol be present

Owing to its property of yielding nascent oxygen, hypochlorous acid is a powerful oxidising agent Thus, when shaken with metallic mercury, an insoluble oxychloride, $HgO\,HgCl_2$, is produced Silver is oxidised similarly to silver oxide, Ag_2O. It oxidises manganous oxide, MnO, into manganese dioxide, MnO_2, while calcium hypochloride changes manganese salts into calcium permanganate, $Ca(MnO_4)_2$

When a solution of hypochlorous acid is treated with certain metallic oxides, such as those of iron, copper, or cobalt, the evolution of oxygen becomes quite rapid, particularly if the solution be warmed. The metallic oxide in these cases acts as a catalytic agent, remaining itself unchanged.

Since hypochlorous acid is capable of giving rise to chlorine as well as oxygen, it acts both as a direct and indirect oxidising agent

The Bleaching Action of Hypochlorous Acid.—Hypochlorous acid is a powerful bleaching agent, though there is some difference of opinion about the manner in which it acts. These differences will be discussed later, but the following points may be noted here :—

Higgins and others hold that hypochlorous acid is a direct bleaching agent, owing its bleaching action to the liberation of nascent oxygen in accordance with the equation

$$HOCl = HCl + O.$$

Higgins (*J.S.C I*, 1912, p. 26) found that hypochlorous acid bleached linen

readily. Its action was more rapid than that of chlorine water. But, if the latter be shaken with calcium carbonate, the bleaching power of the solution is increased greatly, owing to the formation of hypochlorous acid Any substance which accelerates the evolution of oxygen from hypochlorous acid, or its salts, increases its bleaching action, while, on the other hand, bodies which decrease the rate of evolution of oxygen retard the bleaching action These facts point to the conclusion that hypochlorous acid bleaches directly by giving up oxygen The direct bleaching action of hypochlorous acid was investigated also by the present authors, whose results confirmed those of Higgins

It is known that the addition of salt to a solution of hypochlorous acid causes a temporary stimulation of its bleaching activity. This is explained by Higgins (*Bleaching*, p 61) in the following way The equation

$$HOCl+NaCl \rightleftharpoons 2Cl+NaOH$$

is reversible The addition of salt causes the reaction to proceed from left to right, and the production of nascent chlorine gives a sudden stimulation to the bleaching action, but, when a new position of equilibrium is produced, the action ceases The bleaching action of the hypochlorous acid is then due to oxygen directly produced—

$$HOCl=HCl+O$$

Taylor holds a different view He maintains that hypochlorous acid is, of itself, a poor bleaching agent, and is only effective under conditions which bring about its decomposition with the production of nascent chlorine This may be put in another way Higgins believes that hypochlorous acid bleaches because it gives up oxygen, and that hypochlorous acid plays a large part in the bleaching action of bleaching powder; Taylor insists that hypochlorous acid is only a feeble bleaching agent, but what action it exerts is always due to the liberation of chlorine He says, moreover, that when hypochlorous acid is prepared by passing chlorine into water containing calcium carbonate, or when chlorine water is shaken with chalk as in the experiments of Higgins, calcium hypochlorite is produced The reaction

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O$$

is reversible, hence chlorine can be produced

Taylor's statement that hypochlorous acid can dissolve calcium carbonate appears to be based upon the fact that hypochlorous acid prepared by his method of distilling bleaching powder with boric acid, when shaken with this substance, gives a solution containing some calcium

But it has been shown by the authors (*J S.C I.*, 1924, 240T) that Taylor's hypochlorous acid contains traces of free hydrochloric acid and chlorine, and that the distillate has a pH value of from 3 to 4 When shaken with calcium carbonate, it is probable that the hydrochloric acid is neutralised and the chlorine is converted into hypochlorous acid, for if the solution be kept for some days in contact with calcium carbonate, no more calcium goes into solution Moreover, the pH value remains constant at 5·5 to 6 On the other hand, hypochlorous acid solution, if kept alone, acquires an increased power of dissolving calcium carbonate, owing to its gradual decomposition into chlorine and hydrochloric acid

Hypochlorous acid is monobasic, giving rise to salts termed hypochlorites Those of the alkali metals, and alkaline earths, are of great commercial import-

ance They are generally made by passing chlorine gas into a cold solution of the hydroxide of the metal—

$$2NaOH + Cl_2 = NaCl + NaOCl + H_2O,$$
$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + H_2O$$

If the solution of the hydroxide be heated, the reaction goes further and chlorates are formed—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

When hypochlorites are made in this way they are accompanied always by chlorides, from which they are difficult to separate

A solution containing sodium hypochlorite may be made also by treating bleaching powder solution with sufficient sodium carbonate to precipitate all the calcium, and then filtering off the precipitate, or chlorine may be passed into a solution of sodium or potassium carbonate, as in the preparation of eau de Javelle Sodium hypochlorite is prepared also by electrolysing a solution of salt (p 476) When a concentrated cold solution of sodium hydroxide is saturated with chlorine and evaporated at a low temperature, needle shaped crystals of the composition $NaOCl\ 6H_2O$ are deposited Crystalline calcium hypochlorite, $Ca(OCl)_2\ 3H_2O$, free from calcium chloride, can be made in a similar manner

The Mathieson Alkali Co have patented the following method "Solutions of hypochlorous acid prepared by treating water with chlorine, in the presence of calcium carbonate, are extracted at a temperature of from 0° to 5° C with an organic solvent, such as ether, chloroform, tetrachlorethine mixed with a small proportion of alcohol The hypochlorous acid dissolves in the organic solvent and is removed The solution is then treated with about four times the quantity of calcium hydroxide, containing 1 to 3 per cent of free water, required to react completely with the hypochlorous acid present Water is added to the mixture in such quantity that the total free water amounts to from 1 5 to 2 times that required to yield the compound $Ca(OCl)_2 3H_2O$ The mass is extracted with water and the aqueous solution of calcium hypochlorite obtained is evaporated in a vacuum"

The hypochlorites are soluble in water, but insoluble in organic liquids Their aqueous solutions are alkaline in reaction This is due to the fact that they are hydrolysed by water Thus

$$Ca(OCl)_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + 2HOCl$$

Hypochlorites are decomposed readily by acids Even such weak acids as carbonic or boric acids are able to liberate hypochlorous acid from its salts When treated with mineral acids either hypochlorous acid or chlorine is liberated according to the proportion used Thus

$$Ca(OCl)_2 + 2HCl = 2HOCl + CaCl_2,$$
$$Ca(OCl)_2 + 4HCl = 2Cl_2 + 2H_2O + CaCl_2$$

Solutions of hypochlorites have a powerful antiseptic action Bleaching powder (chloride of lime) is used extensively as a disinfectant When brought into contact with proteins, chloramines are produced, together with sodium hydroxide—

$$R\ NH_2 + NaOCl = RNHCl + NaOH$$

Detection and Estimation of Hypochlorous Acid.—Hypochlorous acid may be distinguished from a solution of unchanged chlorine by shaking it with

excess of metallic mercury In the presence of hypochlorous acid, a brownish-yellow precipitate of oxychloride of mercury is produced of the composition $HgOHgCl_2$, while, with chlorine water, a white precipitate of mercurous chloride, Hg_2Cl_2, is formed Hypochlorous acid and chlorine may be quantitatively estimated in presence of each other by Taylor's method (*Bleaching Powder and its Action in Bleaching*, p. 1).

The method depends on the different actions of chlorine and hypochlorous acid on a solution of sodium arsenite. The reactions are—

$$(1)\ As_2O_3+2Cl_2+2H_2O=As_2O_5+4HCl$$
$$(2)\ As_2O_3+2HOCl\ \ =As_2O_5+2HCl$$

For the same amount of arsenite oxidised, twice as much hydrochloric acid, or chloride, is produced in the case of chlorine as in the case of hypochlorous acid. A portion of the solution containing the mixed chlorine and hypochlorous acid is added to an excess of decinormal sodium arsenite solution The mixture is then made up to a definite volume The unoxidised arsenite is determined by titration with decinormal iodine solution and the amount oxidised calculated In another portion the chlorine is estimated by titration with decinormal silver-nitrate solution To titrate the chlorine, Taylor recommends acidifying the solution with nitric acid, adding a little of the silver nitrate, boiling for a minute or two, and filtering a portion of the liquid A little more of the silver solution is added drop by drop to the filtered portion, which is then returned to the bulk, boiled, and filtered again This is continued till the filtered portion gives no further precipitate with silver nitrate.

The following alternative process is given by Treadwell (*Analytical Chemistry*, vol ii p 655) It is based upon the reactions

$$HOCl+2KI=KCl+KOH+I_2,$$
$$Cl_2+2KI=2KCl+I_2$$

A measured volume of decinormal hydrochloric acid is added to a potassium iodide solution. To this, a known volume of the solution to be analysed is added, and the liberated iodine is determined by titration with decinormal thiosulphate solution The colourless solution is then treated with methyl orange and the excess of hydrochloric acid is titrated with decinormal sodium hydroxide. The potassium hydroxide, produced by the action of the hypochlorous acid on the iodide, requires half as much acid for neutralisation as is required of thiosulphate solution to react with the iodine set free by the hypochlorous acid

Example.

V c c of the mixture of chlorine and hypochlorous acid were taken.
t c c of N/10 hydrochloric acid were added
T c c of N/10 thiosulphate were required by the iodine liberated
t_1 c.c of N/10 alkali were required to neutralise the excess of acid.

Then

$t-t_1$ c c N/10 acid were required to neutralise the potassium hydroxide

and

$2(t-t_1)$ c c N/10 thiosulphate were required to react with the iodine formed from the hypochlorite.

Hence

$(t-t_1)\times 0{\cdot}00524$ = grammes HOCl in V c.c of the solution

and

$T-2(t-t_1)\times 0{\cdot}00355$ = grammes Cl in V c c of the solution

Eau de Javelle.—When chlorine is passed into a cold solution of sodium,

or potassium carbonate, the resulting solution contains a mixture of chloride, hypochlorite, and hypochlorous acid. When made from potassium carbonate the solution is known as "eau de Javelle," which is used as a bleaching agent. The reaction takes place in two stages. First, chloride and hypochlorite of potassium are formed, carbon dioxide being liberated—

$$K_2CO_3+Cl_2=KOCl+KCl+CO_2$$

The carbon dioxide does not escape at first As long as any normal potassium carbonate is present, this is converted by the carbon dioxide into bicarbonate—

$$(1)\ K_2CO_3+CO_2+H_2O=2KHO_3.$$

When all of the carbonate is present as bicarbonate the chlorine decomposes this, forming hypochlorous acid and liberating carbon dioxide, which now escapes Thus, effervescence marks the beginning of this stage—

$$KHCO_3+Cl_2=HOCl+KCl+CO_2,$$

or, if excess of chlorine be used—

$$(2)\ K_2CO_3+H_2O+2Cl_2=2KCl+2HOCl+CO_2.$$

A solution containing free hypochlorous acid would be comparatively unstable Hence, the reaction is stopped as soon as free carbon dioxide is liberated, and a little normal carbonate is added to make the solution alkaline In a recent German patent (306193, 20th October 1916) it is claimed that a bleaching liquor, ready for immediate use, can be obtained from sodium carbonate and chlorine, in which between one and two molecules of combined chlorine are present for each molecule of sodium carbonate used, by passing chlorine into a solution of sodium carbonate in the quantity necessary to give equation (1) above, or by passing in two molecules of chlorine for each molecule of sodium carbonate present, and then adding sufficient of the latter to reduce the chlorine content by one-half.

A somewhat similar bleaching liquor can be made by passing chlorine into milk of lime at low temperatures—

$$2Ca(OH)_2+2Cl_2=Ca(OCl)_2+CaCl_2+2H_2O.$$

These bleaching solutions are convenient in many ways They can be made quite easily in any fairly deep tank provided with a stirring apparatus and a lead delivery tube passing to the bottom of the tank and ending in a ring perforated with small holes to distribute the chlorine Or, a small absorption tower may be used The chlorine is introduced at the bottom. As it ascends it meets a descending stream of water containing the alkali. This, on reaching the bottom, is pumped to the top again and the process continued till sufficient chlorination is brought about The following description (U S. Pat. 1481106, 15th January 1924) refers to an apparatus designed by the Mathieson Alkali Works·—

"Milk of lime, caustic soda solution, or like alkaline solution is circulated from a tank, down through a packed tower, and back into the tank Liquid chlorine from a cylinder is passed through coils in the tank, where its evaporation cools the liquid The gas is passed up the tower, where it is rapidly absorbed. A liquid bleach solution of the required strength is in this way readily obtained without the need of external refrigerating apparatus, the evaporating chlorine absorbing all the heat evolved in the reaction. It is of advantage to agitate the liquid in the tank to facilitate uniform cooling by the coils."

Bleaching Powder.—This compound is a double chloride and hypochlorite

of calcium, having the formula $Ca(OCl)Cl$ It is prepared by saturating slaked lime with chlorine gas, when the following reaction occurs :—

$$Ca(OH)_2+Cl_2=Ca(OCl)Cl+H_2O.$$

The lime is spread on the floors of specially constructed chambers and the chlorine led in through an opening at the top under a slight pressure. A glass window is provided, through which the progress of the absorption can be observed. As soon as the yellow colour of the chlorine disappears, more is introduced, the process being repeated till, after occasional turning over, no more gas is absorbed, this point being indicated by the permanent greenish colour of the unabsorbed gas Some fresh lime is then added to absorb this residual chlorine, and the powder is then packed in air-tight drums. The operation is carried out at as low a temperature as possible, to prevent the formation of secondary products such as calcium chlorate, $Ca(ClO_3)_2$

Constitution of Bleaching Powder.—There has been much controversy as to the action of chlorine upon lime, and the constitution of the product produced The question is still far from settled.

It was at one time regarded as a mixture of calcium chloride and calcium hypochlorite, but this hypothesis is not in accordance with its properties, and was soon given up. It is true that its aqueous solution contains both calcium chloride and hypochlorite, but these are formed during the process of solution Calcium chloride is a very deliquescent body, but bleaching powder is not Further, like many other deliquescent compounds, it dissolves readily in alcohol, but no calcium chloride can be extracted from bleaching powder by this solvent Finally, a molecular mixture of calcium chloride and hypochlorite would be much more soluble in water than is bleaching powder

Odling proposed the formula $CaOCl_2$ According to this view, when the powder is treated with water, the following change occurs —

$$2Ca(OCl)Cl=CaCl_2+Ca(OCl)_2$$

The chief difficulties in connection with this formula are that it does not explain the presence of free lime, which is always found in bleaching powder to the extent of 10 to 15 per cent, nor is it quite in accordance with the fact that no calcium chloride can be extracted with alcohol

Stahlschmidt considers that the formation of bleaching powder is represented by the equation

$$3Ca(OH)_2+2Cl_2=2ClOCaOH+CaCl_2+2H_2O.$$

According to this view, it is a mixture of a basic hypochlorite and calcium chloride In presence of water the chloride dissolves, while the basic salt decomposes, yielding hypochlorite and free lime

Attempting to explain the presence of free lime, von Tiesenholt (*J S C I*, 1901, p. 248) regards bleaching powder as being formed in accordance with the equation

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons Ca(OCl)_2+CaCl_2 2H_2O$$

This reaction he regards as reversible, and hence, never complete in either direction Thus free lime would always be present

Ditz (*J.S.C I*, 1901, p. 247), as the result of experiments on the action of dry and moist carbon dioxide on bleaching powder, concludes that the formation of bleaching powder is expressed by the equation

$$2Ca(OH)_2+Cl_2=CaOCa(OCl)Cl\,H_2O+H_2O.$$

This compound, in presence of water, tends to react as follows, producing free lime —

$$CaOCa(OCl)ClH_2O+H_2O=Ca(OH)_2+Ca(OCl)ClH_2O.$$

This free lime is now available for the absorption of more chlorine, in accordance with the first equation. This explains the necessity for the presence of more moisture in the lime than is required to convert it into the hydrate $Ca(OH)_2$, the extent to which this second reaction takes place being governed by this factor. The final reaction is

$$2nCa(OH)_2+(2n-1)Cl_2=(2n-2)Ca(OCl)ClH_2O+CaOCa(OCl)ClH_2O+H_2O.$$

A sample might therefore be produced of any composition between $CaOCa(OCl)ClH_2O$, containing 35·32 per cent. of chlorine, and $Ca(OCl)ClH_2O$, containing 48·96 per cent.

Winteler (*J S C I*, 1903, p. 92) concludes that bleaching powder cannot be represented by a simple formula, but is undoubtedly a mixture of bodies, among which are basic calcium chloride and hypochlorite.

Tarugi (*J S C I.*, 1905, p 25) argues that the formula $CaO_2Cl_2H_2O$ is in accordance with the properties of bleaching powder, pointing out that it quantitatively converts mercury into mercuric chloride, as shown by the equation

$$CaO_2Cl_2+Hg=CaO_2+HgCl_2.$$

He regards the formation of bleaching powder to be due to the presence in slaked lime of calcium peroxide, $CaO_2H_2O_2$, and suggests the following series of reactions —

$$(1)\ 2Cl_2+2H_2O = 4HCl+O_2$$
$$(2)\ CaO_2.H_2O_2+2HCl=CaO_2Cl_2+2H_2O$$
$$(3)\ CaOH_2O+O_2 = CaO_2H_2O_2$$
$$(4)\ CaO_2H_2O_2+2HCl = CaO_2Cl_2+2H_2O$$

Properties of Bleaching Powder.—Bleaching powder is a white amorphous powder which should contain no lumps It has a characteristic chlorine-like smell When exposed to air, it absorbs moisture and carbon dioxide, and deteriorates rapidly It should be kept in air-tight drums. Bleaching powder contains, always, some unchlorinated lime, which may reach 10 per cent Good samples contain from 38 to 39 per cent of chlorine available for bleaching (termed available chlorine) The theoretical yield would be 49 per cent, but 43·5 per cent is the most that can be obtained in manufacture Average samples should not give less than 35 per cent. When bleaching powder is mixed with water, it tends to form a hard cake, unless it is first finely ground and added little by little, or made into a cream with water. When mixed with water it undergoes a molecular transformation, or rearrangement, forming calcium hypochlorite and calcium chloride, which dissolve in the water—

$$2Ca(OCl)Cl=Ca(OCl)_2+CaCl_2.$$

At the same time sufficient calcium hydroxide dissolves to saturate the water, the remainder settling to the bottom of the vessel, forming a precipitate or sludge. This contains, also, any other insoluble impurities of the bleaching powder.

The calcium hypochlorite then undergoes partial hydrolysis in accordance with the equation

$$Ca(OCl)_2+2H_2O\rightleftharpoons Ca(OH)_2+2HOCl.$$

The extent of this hydrolysis is small, since the solution is practically saturated

with calcium hydroxide. But small quantities of hypochlorous acid are actually present

A further reaction may take place also The reaction

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O$$

is also reversible, being governed, chiefly, by the concentration of the solution with respect to calcium hydroxide Thus, traces of free chlorine may also be present A solution of bleaching powder is, in reality, rather complex It contains—

1. Calcium hypochlorite.
2. Calcium chloride
3. Calcium hydroxide
4. Hypochlorous acid formed by hydrolysis
5. Possibly free chlorine
6. Other soluble impurities.

Among the last named may be calcium chlorate, and calcium permanganate. The former would be present, as explained above, if the temperature were allowed to rise too much during chlorination of the lime—

$$6Ca(OH)_2+6Cl_2=5CaCl_2+Ca(ClO_3)_2+6H_2O.$$

Calcium permanganate, $Ca(MnO_4)_2$, is formed if manganese be present as an impurity in the powder Aqueous solutions of bleaching powder frequently develop a pink colour on keeping. This is due to the formation of calcium permanganate

An aqueous solution of bleaching powder is alkaline in reaction. If a stoppered bottle be filled with a freshly prepared solution of bleaching powder, a piece of wet litmus-paper immersed in the solution, and the stopper replaced, it will be noted that very little bleaching action is developed But if the paper be taken out and exposed to air, or if a little acid be added to the solution, or carbon dioxide passed in, the paper becomes bleached very quickly The solution of bleaching powder does not bleach of itself Its bleaching action requires to be developed.

The cotton bleacher uses the carbon dioxide of the atmosphere for this purpose. Exactly how this atmospheric carbon dioxide acts is uncertain This will be discussed fully later But certain facts are beyond dispute

The first action of carbon dioxide on bleaching-powder solution would be to neutralise some of the dissolved calcium hydroxide—

$$Ca(OH)_2+CO_2=CaCO_3+H_2O.$$

If the dissolved calcium hydroxide were neutralised, the calcium hypochlorite would be next decomposed and hypochlorous acid liberated—

$$Ca(OCl)_2+CO_2+H_2O=CaCO_3+2HOCl.$$

In either case calcium carbonate is formed and the natural development of the bleaching action of bleaching-powder solution is always accompanied by the precipitation of this body, either on the goods, or the sides and bottom of the container

Now, a bleaching-powder solution remains alkaline throughout Hence, the whole of the calcium hydroxide cannot be removed, and it follows that calcium hypochlorite cannot be decomposed, because the calcium hydroxide would take up the carbon dioxide first. Thus, the mere reduction of the amount of calcium

hydroxide present in the solution, without neutralising it completely, is sufficient. In fact, mere traces of carbon dioxide are able to develop the bleaching action.

Probably the explanation is to be found in the hydrolysis into calcium hydroxide and hypochlorous acid. This hydrolysis only proceeds to a limited extent, being inhibited as soon as a certain amount of lime is formed, equilibrium being set up. Now very little carbon dioxide is sufficient to destroy this state of equilibrium and encourage further hydrolysis with the liberation of more hypochlorous acid. This also explains the practice of adding lime water to retard the bleaching activity of a bleaching-powder solution. The production of calcium carbonate is sufficiently evident in the scale which is formed in the apparatus and pipes in the bleaching process. It will be noted that, according to this view, the bleaching action of bleaching powder is due to hypochlorous acid, at any rate when only limited quantities of acid are present.

This raises the question referred to on p. 429 as to the bleaching power of hypochlorous acid in comparison with that of chlorine. There has been much discussion as to whether bleaching powder owes its action to the development of hypochlorous acid or chlorine, or to both.

Taylor (*J S C.I*, 1910, pp 693, 1302) claimed that, when the bleaching action is developed by means of atmospheric carbon dioxide, the active bleaching agent is always chlorine, hypochlorous acid being only produced by excess of carbonic acid, which acts just like any other acid. It has been stated already that excess is never present.

According to Taylor, air free from carbon dioxide is without action on bleaching powder, merely driving out any chlorine or hypochlorous acid that it may contain, the hypochlorous acid being formed by hydrolysis. If moist air containing carbon dioxide is passed over bleaching powder only chlorine is obtained. If the air be dry this action only proceeds as long as the powder contains moisture, becoming gradually slower as this is expelled But with both dry and moist carbon dioxide only chlorine is produced so long as the carbon dioxide is not present in large excess

Taylor explains the action of ordinary moist air on bleaching powder as follows The carbon dioxide unites with the free lime, and, as this gradually diminishes, the reversible equation

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O$$

proceeds from right to left. The action of a stream of carbon dioxide is different. Taylor showed that it can liberate a sensible amount of hydrochloric acid from calcium chloride, in fact that the equation

$$CaCO_3+2HCl \rightleftharpoons CaCl_2+H_2CO_3$$

is reversible. If well washed carbon dioxide be bubbled through distilled water containing methyl orange, there is a distinct alteration of colour, although the mixture does not turn red. If, however, calcium chloride be present, a distinct acid reaction is produced. It has been objected that the effect of carbon dioxide on methyl orange, in the presence of calcium chloride, is due probably to increased ionisation of the carbonic acid and not to liberation of hydrochloric acid.

The authors have repeated the experiment, using a "universal indicator." They found that the pH value indicated was exactly the same when a stream of carbon dioxide was passed through distilled water, both with and without calcium chloride. In both cases the same increase in acid reaction was observed.

But, assuming that Taylor's view is correct, even a very small quantity of

hydrochloric acid would be sufficient to explain the action of carbon dioxide on bleaching powder, as shown by the following equations —

$$CaCl_2+H_2CO_3=CaCO_3+2HCl,$$
$$Ca(OCl)_2+H_2CO_3=CaCO_3+2HClO,$$
$$2HCl+2HClO=2H_2O+Cl_2.$$

When this cycle has been completed and the chlorine is removed the carbonic acid acts again as before until the bleaching powder is almost entirely decomposed

With a solution of bleaching powder the quantity of hypochlorous acid driven out by carbon dioxide-free air is greater than in the case of powder This agrees with the view that it is produced by hydrolysis. The liberation of chlorine depends upon the reversibility of the reaction

$$2Ca(OH)_2+2Cl_2\rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O.$$

The presence of calcium chloride in bleaching powder is explained by the action of moisture

This condition of equilibrium depends upon the presence of free lime which, according to Taylor, is always present in bleaching powder Whenever this is removed or diminished, as by the action of carbon dioxide, the reaction proceeds in the reverse direction till equilibrium is again established Thus it must be chlorine and not hypochlorous acid which is the active bleaching agent In support of his theory, Taylor proved that the addition of calcium chloride, or sodium chloride, to a solution of bleaching powder caused an immediate increase in its bleaching activity This can only be because it destroys the equilibrium of the equation

$$2Ca(OH)_2+2Cl_2\rightleftharpoons Ca(OCl)_2+CaCl_2+2H_2O,$$

and thus causes the liberation of chlorine This reversion is more marked when some of the calcium hydroxide has been removed from the solution

Von Tiesenholt suggested another view. Although he agrees that the reversibility of the equation given above causes the liberation of chlorine, he considers that hypochlorous acid is liberated, also, by the action of atmospheric carbon dioxide This then reacts with calcium chloride with the liberation of chlorine Thus

$$Ca(OCl)_2+H_2CO_3=CaCO_3+2HOCl,$$
$$CaCl_2+2HOCl=Ca(OH)_2+Cl_2$$

Higgins (*J.S.C.I.*, 1911, p. 485) showed that when calcium chloride is added to lime water the rate at which it attracts carbon dioxide from the air is increased He thought that this fact probably accounts for the increase in bleaching activity observed by Taylor, when calcium chloride is added to bleaching-powder solution Equivalent quantities of calcium and sodium chlorides have exactly the same effect He gives the following equations as representing the action of carbon dioxide on bleaching powder —

(1) $Ca(OCl)_2+CO_2+H_2O=CaCO_3+2HOCl$
(2) $2HOCl+CaCl_2+CO_2=CaCO_3+2Cl_2+H_2O.$

The reaction of equation (2) is reversible, and this accounts for Taylor's results In bleaching with bleaching-powder solution, according to Higgins, hypochlorous acid enters into the bleaching action, and as much nascent chlorine as is supplied by equation (2), the carbon dioxide being obtained from the air

There are thus two distinct chemical theories of the action of carbon dioxide on bleaching powder. The discussion was then directed towards the relative bleaching powers of hypochlorous acid and chlorine.

Higgins, as noted above, observed that free chlorine had little bleaching effect on the colouring matters of linen compared with hypochlorous acid. According to his views (*J.S.C.I.*, 1912, p. 26), hypochlorites bleach because of the readiness with which they give up nascent oxygen Bodies which accelerate the evolution of oxygen from hypochlorites (or peroxides) increase the bleaching power of the solution, while, on the contrary, anything which decreases the rate of evolution of oxygen delays the bleaching action. These facts point to the conclusion that the action of hypochlorites in bleaching is identical with their action on exposure to air or in contact with a catalytic agent, such as copper oxide. The action of metallic oxides on hypochlorites is quite analogous to that on chlorates. Thus, bleaching-powder solution oxidises manganese salts to permanganates, with chromic oxide it gives a mixture of oxygen and chlorine, while a chromate remains in solution He showed further (*J.S C.I.*, 1912, p 486, 1913, p. 350) that the stimulating action of chlorides is only immediate and of short duration, arguing that it cannot, therefore, depend upon the reversion,

$$NaOCl+NaCl+H_2O \rightleftharpoons 2NaOH+Cl_2,$$

for the following reasons (1) Sodium fluoride or calcium chloride have the same effect on sodium hypochlorite as sodium chloride, (2) if the action were due to the reversion of the above equation there should be a steady liberation of chlorine as long as any sodium hypochlorite remained; (3) the equation gives no explanation of the fact that chlorides stimulate the action of both hypochlorous acid and chlorine water

If sodium chloride, calcium chloride, or hydrochloric acid be added to chlorine water, the colour and smell of free chlorine are greatly increased. It has been shown that chlorine is less soluble in a solution of salt than in water. Hence, salts which lower the solubility of chlorine also stimulate bleaching. Higgins suggests that the action is explained by the following equations .—

$$(1)\ H_2O+Cl_2 \rightleftharpoons HOCl+HCl$$
$$(2)\ NaOH+Cl_2 \rightleftharpoons HOCl+NaCl.$$

On adding hydrochloric acid to chlorine water, reaction (1) is driven from right to left, free chlorine being liberated till equilibrium is established, while addition of salt gives equation (2) a stimulus in the same direction till equilibrium is again established The chlorine produced is nascent, and in this state has a bleaching action which free chlorine does not possess

With hypochlorite solutions the reactions are quite similar—

$$(1)\ Ca(OCl)_2+2H_2O \rightleftharpoons Ca(OH)_2+2HOCl$$
$$(2)\ CaCl_2+2HOCl \rightleftharpoons Ca(OH)_2+2Cl_2.$$

The extent of the reaction is determined by the free calcium hydroxide This effect is initial only, and independent of the main action of hypochlorous acid, which is due to oxygen—

$$HOCl=HCl+O.$$

Confirmation of the view, that the chief action is due to the liberation of oxygen from hypochlorous acid, was found by Higgins in the fact that he was able to show (*J.S.C I.*, 1913, p 1064) that in the case of weak solutions, at any rate, the reaction is unimolecular, as is the decomposition of hydrogen peroxide, or

bleaching-powder solution under the influence of a catalytic agent which causes the evolution of oxygen.

Further experiments may also be referred to Higgins (*J S.C.I.*, 1913, p 1153) is of opinion that excess of boric acid liberates hypochlorous acid from bleaching-powder solutions. Such a solution has, he found, energetic bleaching action. Excess of hydrochloric acid gives free chlorine and weak bleaching properties. But if calcium carbonate be added to the solution, hypochlorous acid is regenerated and the bleaching power restored Even in the presence of alkali there is still some free hypochlorous acid present He agrees that in bleaching, hydrochloric acid gradually accumulates and reacts with the hypochlorous acid, giving chlorine—

$$HOCl+HCl \rightleftharpoons H_2O+2Cl.$$

This action is reversible, the reverse direction representing the behaviour of chlorine water, and in each case, when equilibrium occurs, bleaching ceases (*J.S C I.*, 1914, p 1152) When a hypochlorite is used for bleaching, the hydrochloric acid produced is used in liberating more hypochlorous acid The removal of free hydrochloric acid from either chlorine water or hypochlorous acid by addition of calcium carbonate has been shown experimentally to accelerate the bleaching action

Taylor's observation (*J.S.C I*, 1914, p 308), that there is always a certain amount of residual colour in cotton treated with hypochlorous acid or chlorine water, is explained by this state of equilibrium; when calcium carbonate is added, the cotton is completely bleached The colouring matters of brown linen and of boiled cotton are at once partially bleached on immersion in chlorine water, but prolonged treatment has very little further effect The action of bleaching-powder solutions on cotton dyed with direct and basic dyestuffs has been examined, in a number of cases the solutions to which hydrochloric acid was added caused a change of colour, whilst when boric acid was added no such change was observed In the majority of cases the solutions containing hydrochloric acid had the more bleaching action, with alizarin sapphirole, however, the reverse was the case

The views of Higgins are summed up as follows in Vol II of *Annual Reports in Applied Chemistry*, p 163 —

It seems to be established that the bleaching action of hypochlorous acid is due to (1) the direct production of nascent oxygen from hypochlorites, and (2) the production of nascent chlorine by the action of the hypochlorous acid on chlorides

But Taylor (*J. Soc. Dyers and Col*, 1922, p. 93) still maintains that the active bleaching properties generally attributed to hypochlorous acid are, for the most part, imaginary, and are not characteristic of the pure substance itself In support of this view he records the following experiments —

Comparative experiments with solutions of chlorine and hypochlorous acid, of the same oxidising strength and various colouring matters, have shown that in all cases the chlorine attacked the colouring matter more rapidly than hypochlorous acid The stimulation of the action of hypochlorous acid observed on the addition of hydrochloric acid is due to the liberation of chlorine But other acids, such as sulphuric, nitric, phosphoric, and acetic, stimulate the action, though to a much less marked degree A solution of hypochlorous acid in water is only very slightly ionised The stimulating effect of acids, other than hydrochloric acid, is probably due to increase in hydrogen ions

When calico dyed with indigo or turkey red is placed in moderately strong

solutions of chlorine and hypochlorous acid of the same oxidising power, the bleaching is at once seen to proceed more rapidly in the chlorine water, but later the hypochlorous acid becomes more active, and may ultimately catch up with the chlorine water. Taylor explains this as being due to the equations

$$(1)\ HClO = HCl + O$$
$$(2)\ HClO + HCl = H_2O + 2Cl.$$

That is, the subsequent acceleration is really due to chlorine.

The bleaching action of dilute chlorine water is also stimulated by the addition of hydrochloric acid This is intelligible, for the action of chlorine on water is twofold, viz (1) solution of chlorine, and (2) decomposition into hypochlorous acid in accordance with the reversible equation

$$H_2O + Cl_2 \rightleftharpoons HOCl + HCl.$$

The addition of hydrochloric acid would tend to make the reaction proceed from right to left of the equation, and the addition of just the right amount of acid ought to produce a mixture which would behave exactly like dilute chlorine water Taylor found that if a solution of N/500 hypochlorous acid be mixed with half its volume of N/500 hydrochloric acid, the bleaching action of the resulting mixture appears to be absolutely identical with N/500 chlorine water mixed with half its volume of water. It should be noted that a normal solution of hypochlorous acid, if measured by its oxidising power only, would contain $\frac{HOCl}{2}$, *i e* 26·25 grammes per litre, so that a given volume of N/500 hydrochloric acid would contain twice as many molecules as the same volume of N/500 hypochlorous acid Consequently, if the two dilute acids were mixed in equal volumes, the resulting mixture would not behave like chlorine water, but like chlorine water to which some hydrochloric acid has been added.

The conclusions of Higgins as to the greater bleaching action of hypochlorous acid are vitiated, according to Taylor, by the fact that hypochlorous acid can only be obtained from a mixture of bleaching powder and boric acid by his process of distillation A mixture of the two always contains, not only free chlorine, but unaltered calcium hypochlorite. He maintains that if hypochlorous acid were distilled off, Higgins' results and his would point to the same conclusion, namely, that, considered simply as a bleaching agent, chlorine is more active than hypochlorous acid.

Some interesting results of the action of chlorine water on litmus are also recorded by Taylor (*loc cit*) When 40 to 50 c.c. of very dilute chlorine water, *e g* N/1000 to N/2000, are added to a few cubic centimetres of fresh litmus solution, the liquid becomes, at once, bright red in colour, but in a few seconds changes to purple, and then, if sufficient chlorine water be added, slowly disappears The bright red colour is due to the hydrochloric acid, hypochlorous acid has very little, if any, reddening effect on litmus Hence the change from the acid bright red colour back to the purple must be accompanied by the disappearance of hydrochloric acid.

Taylor suggests that the free chlorine present is immediately used up in bleaching some of the litmus. This enables the reaction

$$H_2O + Cl_2 \rightleftharpoons HOCl + HCl$$

to be reversed with the production of more free chlorine If this be correct, an important deduction follows, namely, that the view that chlorine bleaches by

decomposing water and liberating oxygen cannot be correct In the case of litmus, at any rate, chlorine acts directly upon the colouring matter

In connection with the relative bleaching powers of hypochlorous acid and chlorine some experiments made by the authors (*J S C I*, 1923, 2T) may be quoted

Boiled cotton (100 grammes) was bleached with (1) hypochlorous acid, (2) bleaching powder solution acidified with boric acid, (3) bleaching powder solution exposed to air, (4) bleaching powder solution acidified with hydrochloric acid Hypochlorous acid was prepared by passing chlorine gas into water containing chalk in suspension, the solution being kept in contact with chalk till used The strengths of the solutions were adjusted to 1 gramme of available chlorine per litre, and the same volume of liquor was used throughout

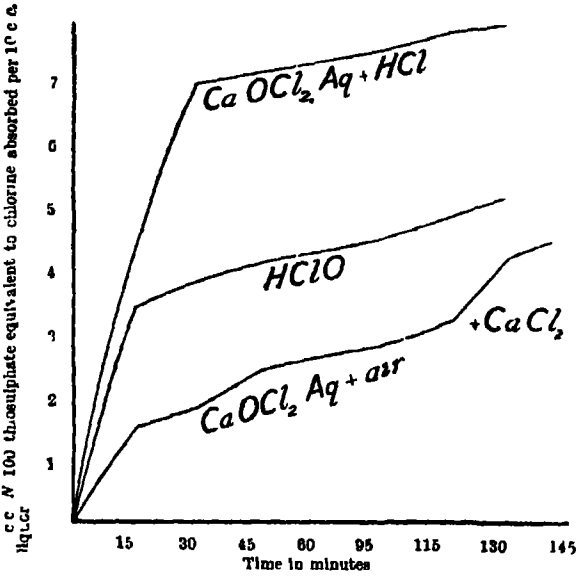


FIG. 148A.

The rate of absorption of chlorine was found to be most rapid in the case of bleaching powder acidified with hydrochloric acid, and slowest with bleaching powder solution and air The rates of absorption for hypochlorous acid and bleaching powder solution acidified with boric acid were identical and intermediate between the other two

In every case there is a comparatively rapid initial absorption, which gradually becomes slower and more regular This is shown in fig 148A which gives the rate of absorption of chlorine in terms of N/100 thiosulphate In the case of bleaching powder solution and air the stimulating effect of adding calcium chloride is also indicated An immediate absorption of chlorine is caused, but the rate quickly falls again

The rate of apparent bleaching always follows in the same order as the rate of absorption of chlorine When boiled cotton is put into hypochlorous acid solution there is an immediate bleaching action The cotton appears to be bleached in about fifteen minutes at the point in the curve where the rate of

absorption changes, but the last traces of colouring matters require some time to remove. The action of bleaching powder acidified with hydrochloric acid is similar but much more rapid, while that of bleaching powder exposed to air is slow and regular. Stimulation with calcium chloride or acid increases both the rate of absorption and the bleaching effect. The addition of hydrochloric acid to hypochlorous acid gives exactly the same effect.

Ristenpart (*J. Text. Inst*, 1924, T 157) states that the addition of acid to a bleaching-powder solution accelerates the rate of bleaching only till all the hypochlorite is decomposed into hypochlorous acid, *i.e* in accordance with the equation

$$Ca(OCl)_2+2HCl=CaCl_2+2HOCl.$$

Further addition of acid only causes liberation of chlorine, which has not the bleaching power of free hypochlorous acid

The Action of Acids on Bleaching Powder.—Taylor and Bostock (*J S.C.I.*, 1912, p 228) investigated the action of various acids on bleaching powder In making the experiments 10 grammes of bleaching powder were rubbed with water and then the desired volume of acid was added slowly from a burette, the mixture being shaken continually to ensure equal distribution. The whole of the mixture was then distilled from a flask of about 1 litre capacity, the vapours being passed through a small condenser A few drops of the distillate were rejected and then 20 c c collected The proportions of chlorine and hypochlorous acid were determined in 10 c c of the distillate by the sodium arsenite method already described. The results of these experiments showed

1 When bleaching powder, mixed with thirty times its weight of water, is distilled with sulphuric, hydrochloric, or nitric acid in quantity slightly greater than is required to neutralise the free lime present, hypochlorous acid mixed with a small quantity of free chlorine is evolved When the acid is in sufficient quantity to neutralise all the free lime and to decompose the whole of the hypochlorite theoretically present, the proportion of free chlorine is considerably greater When the amount of acid is further increased, the hypochlorous acid produced diminishes rapidly, and very soon nothing but chlorine is evolved There is not a great difference in the action of the three acids named

2 Acetic and phosphoric acids behave much alike, but they differ considerably, as would be anticipated, from the three acids above mentioned. Even with comparatively large amounts of these acids the proportion of hypochlorous acid evolved does not fall much below 50 per cent

3 When bleaching powder is distilled with boric acid and a sufficient amount of water, almost pure hypochlorous acid is produced, and there is very little difference in the result if the boric acid used is as much as three times the weight of the bleaching powder This is recommended as a convenient method of preparing a solution of hypochlorous acid

4 When carbon dioxide is bubbled through a mixture of bleaching powder and water at different temperatures, whilst at the ordinary temperature nothing but chlorine is evolved, as soon as the liquid becomes warm, hypochlorous acid begins to come off. The proportion of hypochlorous acid increases as the temperature rises, and when the liquid boils it is practically pure, hardly any free chlorine being evolved. It is suggested that this is strong evidence in favour of Taylor's view that the action of carbonic acid on bleaching powder at the ordinary temperature is like that of other acids.

5. When boric acid is added to a solution of bleaching powder and air free from carbon dioxide is passed through at the ordinary temperature, a mixture

of chlorine and hypochlorous acid is swept out, containing a considerable excess of the former The boric acid simply unites with the free lime, and this allows the reverse action to proceed, free chlorine being produced If any other acid be added to a solution of bleaching powder in quantity just sufficient to neutralise the free lime the passing of air free from carbon dioxide through the solution gives a similar result

It is evident that when a mineral acid is added to a solution of bleaching powder in sufficient quantity to just neutralise the free lime present, the condition necessary for the liberation of hypochlorous acid by hydrolysis is established, and if the acid be very cautiously increased to neutralise the calcium hydrate as it is produced, only hypochlorous acid is formed in accordance with the equation

$$Ca(OCl)_2+2H_2O \rightleftharpoons Ca(OH)_2+2HOCl$$

Further addition of acid causes the calcium hypochlorite to be decomposed—

$$Ca(OCl)_2+2HCl=CaCl_2+2HOCl$$

As soon as any excess of acid is present above that required to decompose the hypochlorite it reacts with the hypochlorous acid present, giving chlorine—

$$HCl+HOCl=H_2O+Cl_2$$

With excess of sulphuric acid the reactions would be

$$Ca(OCl)_2+CaCl_2+2H_2SO_4=2CaSO_4+2HCl+2HOCl,$$
$$2HCl+2HOCl=2H_2O+2Cl_2$$

Acids are used in bleaching for this purpose, namely, to accelerate the bleaching action, although, as a rule, the bleacher relies upon atmospheric carbon dioxide

In this connection the action of sodium bicarbonate is interesting Higgins (*J Soc Dyers and Col*, 1912, p 30) noted that when sodium bicarbonate is added to a solution of calcium chloride, calcium hydrogen carbonate, $Ca(HCO_3)_2$, is first produced This decomposes, giving off carbon dioxide and precipitating calcium carbonate—

$$CaCl_2+2NaHCO_3=2NaCl+Ca(HCO_3)_2,$$
$$Ca(HCO_3)_2=CO_2+CaCO_3+H_2O$$

If bleaching powder be used instead of calcium chloride, the carbon dioxide combines with the free calcium hydroxide in the solution, precipitating it as calcium carbonate This, by allowing hydrolysis to take place, gives an active bleaching liquor

In MacIlwaine's process (*J S C I*, 1915, p 75) the same principle is involved The material to be bleached is impregnated with a solution of sodium bicarbonate and then with the hypochlorite bleaching liquor, or the order of impregnation may be reversed Impregnation may be assisted by mechanical pressure It is claimed that the active bleaching agent is liberated in the body of the fibre

Acids are generally used for another purpose The action of carbon dioxide gives rise to insoluble calcium carbonate, which remains deposited on the goods This, if left, causes a harsh feel Being insoluble in water, it must be removed by means of an acid bath or sour This produces a soluble calcium salt capable of being removed by washing In this respect it is important to remember that calcium chloride is more soluble in water than calcium sulphate, and that where harshness has to be specially guarded against, hydrochloric acid should be employed

The Action of Alkalis of Bleaching-powder Solution.—Alkalis have an

effect on bleaching-powder solutions exactly opposite to that of acids If lime water be added, the equilibrium of the equation

$$Ca(OCl)_2+2H_2O \rightleftharpoons Ca(OH)_2+2HOCl$$

is destroyed, the increase in the constituent which determines stability causing the reaction to proceed in the reverse direction, and thus inhibiting the bleaching action. If we take the equation

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O$$

the result would be the same

Other alkalis, such as sodium hydroxide or carbonate, act in the same way. Just as acids may be used to accelerate or develop the bleaching action, so also alkalis may be employed to retard or inhibit it.

In general, anything which increases the alkalinity retards bleaching, while diminution of alkalinity accelerates it.

An interesting illustration of this is found in the action of a solution of magnesium sulphate This reacts with the calcium hydroxide forming magnesium hydroxide, which is insoluble in water—

$$Ca(OH)_2+MgSO_4=Mg(OH)_2+CaSO_4.$$

The addition, therefore, of this salt reduces the alkalinity and accelerates bleaching

The Action of Metals and their Oxides on Solution of Bleaching Powder.—Many metals or their oxides act as catalytic agents when placed in a solution of bleaching powder, causing rapid decomposition Dobbin and White (*J.S C I.*, 1903, p 134) found that the metals could be divided into two classes

Certain metals, including iron, nickel, copper, cobalt, and, to a less extent, tin, are attacked rapidly by bleaching-powder solution at ordinary temperatures, with formation of their hydrated oxides and liberation of oxygen. When the oxide has been formed the decomposition may go on indefinitely. Other metals, including magnesium and aluminium, on the contrary, liberate hydrogen and are changed into hydroxides

Higgins (*J S C I.*, 1911, p 1296) gives the following details Copper hydroxide, added to a solution of bleaching powder, causes effervescence, due to the liberation of oxygen Finely divided copper does not give immediate evolution of oxygen, but it soon becomes coated with copper oxide and then the oxygen is liberated, thus proving that it is the oxide and not the metal which acts as the catalytic agent. Copper soaps act in the same way, oxides being the first product of their decomposition. Zinc dust liberates hydrogen till it is all converted into zinc hydroxide, $Zn(OH)_2$, when the action ceases. Precipitated zinc hydroxide has no action Zinc salts added to a bleaching liquor act like magnesium sulphate, since zinc hydroxide is insoluble, that is, they give a more active liquor. In the case of brass the zinc constituent, therefore, has no deleterious action

These facts not only have an important bearing on the storing of bleaching powder and its solutions, but indicate strongly the necessity for avoiding the presence of metallic particles in the bleaching tanks or on the goods. When cotton is brought into contact with iron during bleaching, this reaction at once takes place, and nascent oxygen is liberated. This either directly attacks the cellulose, forming oxycellulose, or first forms chlorate, which in its turn reacts in the same way on the cotton The result is always tendering and subsequent weak spots or holes. It may, however, be noted that iron quickly becomes

coated with calcium carbonate in contact with bleaching-powder solutions, so that the use of iron apparatus is not absolutely impossible, as is the case with sodium hypochlorite.

Not only do metals act in this way, but the same results are produced by the oxides themselves. When a bleaching-powder solution is boiled with a little freshly made cobalt oxide, oxygen is rapidly liberated, the oxide playing the part of a catalytic agent or oxygen carrier It is first oxidised at the expense of the bleaching powder into the trioxide Co_2O_3 This compound then gives up part of the oxygen, reproducing the monoxide, which again goes through the same cycle of changes These reactions are shown in the equations

$$Ca(OCl)Cl+2CoO=Co_2O_3+CaCl_2,$$
$$2Co_2O_3=4CoO+O_2$$

The same result may be obtained by passing chlorine through hot milk of lime containing cobalt oxide in suspension Iron and other oxides act in an exactly similar manner, and iron oxide constitutes a very real danger in bleaching Goods that are iron-spotted before chemicking are generally over-bleached, owing to this catalytic action of iron oxide This impurity must be particularly avoided in both the powder and the goods Higgins (*J.S.C.I.*, 1911, p 189) has recorded an interesting case of local over-bleaching and tendering (due to oxycellulose) caused by spots of copper oxide, which owed their presence to the use of an acid lubricating oil This had dissolved copper from the brass parts of the loom When the goods were boiled, copper soap and ultimately copper oxide were produced The latter compound acting as a catalytic agent, in the manner described above, had caused the production of oxycellulose in the chemic Iron oxide is sometimes held to be accountable also for the pinkish colour which is developed by bleaching-powder solutions, though, as noted above, it is probably due to manganese.

Antichlors.—When it is necessary to ensure absolute freedom from chlorine in bleached goods they are treated with a dilute solution of sodium thiosulphate, $Na_2S_2O_3$, and washed Bleaching powder gives up its chlorine to sodium thiosulphate, forming sodium hydrogen sulphate and hydrochloric acid—

$$Na_2S_2O_3+4Cl_2+5H_2O=2NaHSO_4+8HCl$$

A solution of sodium bisulphite or sulphite may be used in the same way—

$$2NaHSO_3+2Cl_2+2H_2O=Na_2SO_4+4HCl+H_2SO_4,$$
$$Na_2SO_3+Cl_2+H_2O=Na_2SO_4+2HCl$$

Valuation of Bleaching Powder.—The value of a sample of bleaching powder is measured by the percentage of "available" chlorine it contains By available chlorine is meant the chlorine capable of being liberated by an acid, *i.e.* available for bleaching Its measurement is based upon the power which chlorine has of liberating iodine from a solution of potassium iodide, in accordance with the reaction

$$2KI+Cl_2=2KCl+I_2.$$

This liberated iodine is then estimated by means of a standard thiosulphate solution, and from the quantity of iodine found the equivalent of chlorine is calculated, and thus the percentage obtainable from the bleaching powder. Good samples of bleaching powder contain 38 per cent. of available chlorine The following are the details of the method generally used :—

About 10 grammes of the powder are weighed and mixed with water in a

mortar till a thin cream is produced. After allowing the mixture to stand for a few minutes, the liquid is decanted off into a litre flask, so as to leave the undissolved residue in the mortar. This is ground again with water and decanted, the process being repeated till the whole of the powder has been transferred to the flask. The solution is then made up to 1 litre with water and thoroughly mixed After shaking, and before the sediment has time to settle, 25 c.c are withdrawn with a pipette and placed in a stoppered bottle About 1 gramme of solid potassium iodide is then added, and a slight excess of dilute sulphuric acid. This liberates the chlorine, which, in its turn, decomposes the potassium iodide, setting free its equivalent of iodine, as shown in the above equation. A burette is now filled with decinormal sodium thiosulphate solution, which is now run in, replacing the stopper and shaking the bottle after each addition, till the mixture has a faint yellow colour. A drop of starch solution is then added and the addition of the thiosulphate solution continued till the blue colour of the iodide of starch is discharged This will take place when the whole of the iodine has been converted into sodium iodide, in accordance with the equation

$$2Na_2S_2O_3+I_2=2NaI+Na_2S_4O_6.$$

Each cubic centimetre of thiosulphate solution used corresponds to 0 00355 gramme of chlorine, and hence the value of the bleaching powder can be calculated

Decinormal sodium thiosulphate solution is prepared by dissolving 24·8 grammes of pure recrystallised thiosulphate in distilled water, and making the solution up to 1 litre

The starch solution may be made by pouring a cream, made by mixing 1 gramme of soluble starch with water, into 100 c c of boiling water

Instead of sodium thiosulphate a decinormal solution of arsenious acid may be employed. This body is oxidised by chlorine into arsenic acid in accordance with the equation

$$2Ca(OCl)Cl+As_2O_3=As_2O_5+2CaCl_2$$

The arsenious acid is run in from a burette until a drop of the solution removed with a glass rod no longer turns iodised starch-paper blue This paper is made by dissolving a little potassium iodide in starch solution, and dipping a strip of filter-paper into the solution and drying it If a decinormal solution of arsenious acid be used, each cubic centimetre used corresponds to 0·00355 gramme of chlorine.

The arsenious acid solution is prepared in the following manner Exactly 4·95 grammes of pure arsenious oxide are placed in a litre flask with 25 grammes of crystalline sodium carbonate and about 200 c c of distilled water The mixture is boiled gently with shaking until solution is complete, after which it is cooled and made up to a litre with water The titration can be simplified by using indigo sulphate or indigo carmine as an indicator, this body being readily decolorised by chlorine In this case, however, the operation is reversed A measured quantity, say 25 c c of the arsenious acid solution, together with a little hydrochloric acid, are placed in a flask, together with a drop of indigo solution. The bleach liquor is now run in from a burette with shaking till the colour is just discharged, or a yellowish tint obtained.

Among other methods of testing bleaching powder, the following may be noted: Dienert and Wandenbulcke (*J. Text Inst.*, 1923, T75) titrate with arsenious oxide solution in the presence of ammonium sulphate, which prevents the formation of iodate. One c.c. of the aqueous solution of the bleaching

powder is diluted to a litre, 2 grammes of ammonium sulphate added, followed, after shaking the mixture, by a few crystals of potassium iodide and a little starch solution The liberated iodine is then titrated with an alkaline standard solution of arsenious oxide, 1 c.c of which is equivalent to 1 mgm. of available chlorine.

Kertesz (*J Soc Dyers and Col.*, 1924, p. 94) recommends the use of an alkaline solution of sodium nitrite instead of arsenious oxide It is made by dissolving 2·6 grammes of sodium nitrite and 20 grammes of sodium bicarbonate in water and diluting the solution, with water, to a litre. It may be standardised by running it into an acidified solution containing a known volume of N/10 permanganate solution till the colour disappears, and titrating back the slight excess The reaction is in accordance with the equations

$$NaNO_2+HOCl=NaNO_3+HCl,$$
$$NaNO_2+Ca(OCl)Cl=NaNO_3+CaCl_2.$$

The results are not affected by chlorates or ferric compounds Traces of ammonia have no influence, but the end point is spoiled by appreciable quantities, such as may occur in sodium bicarbonate. If the bleaching powder contain much calcium hydroxide, sufficient sodium bicarbonate must be added to convert it into calcium carbonate The end point of the reaction is indicated sharply by the blue colour of iodide of starch paper or of zinc-iodide-starch solution In the presence of ammonia no end point is obtained with starch iodide paper This fact can be utilised as a delicate test for ammonia, of which 1 part in 2 to 3 millions can be detected in this way

When it is necessary to determine chlorides, the method of Makamura may be used The available chlorine as hypochlorite is first determined by titration The hypochlorite is next converted into chloride by treating another portion of the solution with hydrogen peroxide, and the percentage of chlorine present as chloride is found by difference After treatment with hydrogen peroxide, the solution is boiled to expel the excess of this body, and is then cooled and titrated with decinormal silver-nitrate solution or the silver chloride collected and weighed The total chlorine may be determined also by treating the solution with excess of ammonium hydroxide and boiling—

$$3Ca(OCl)_2+4NH_3=3CaCl_2+2N_2+6H_2O.$$

Chlorine present as chlorate may be determined in the following manner When chlorates are heated with hydrochloric acid chlorine is evolved Thus

$$Ca(ClO_3)_2+2HCl=CaCl_2+2HClO_3,$$
$$2HClO_3+10HCl=6H_2O+6Cl_2$$

Hypochlorites are decomposed also in the same way, but the chlorine produced can be determined by titration with sodium thiosulphate and allowed for Hence, if a known weight of bleaching powder, or a definite volume of its solution be heated with excess of hydrochloric acid and the resulting chlorine led into a solution of potassium iodide, the total chlorine due to hypochlorites and chlorates can be obtained by titration. The following method is given by De Keghel (*Les Produits de Blanchiment*, p. 79) :—

The apparatus used is illustrated in fig. 149. Twenty-five c c. of the bleaching-powder solution and a small fragment of magnesite are placed in the flask A, and in the retort B, diluted potassium-iodide solution, till the end of the delivery tube is immersed as shown in the illustration. Twenty-five c c of hydrochloric

acid are then added to the contents of the flask and the mixture is heated till the chlorine is expelled The receiver B should be immersed in cold water. The retort is then withdrawn, its contents washed into a flask, and the liberated iodine is determined by titration with decinormal sodium thiosulphate solution.

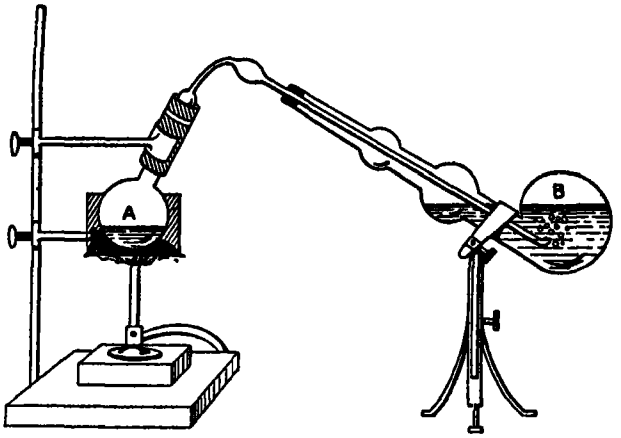


FIG. 149 —Apparatus for determination of chlorates.

Bleaching powder is rarely adulterated, although it may be poor in available chlorine.

Iron oxide is sometimes present in distinct quantities in bleaching powder. The danger attached to its presence has already been mentioned.

The following examples of commercial bleaching powders are taken from Thorpe's *Dictionary of Chemistry* .—

	A.	B.	C.
	p c.	p c.	p.c.
Available chlorine	37 00	28 30	36 00
Chlorine as chloride	0 35	0 59	0 32
Chlorine as chlorate	0·25	0·08	0·26
Lime	44 49	43·34	44·66
Magnesia	0 40	0 31	0 43
Peroxide of iron	0 05	0·04	0 02
Alumina	0 43	0 41	0·33
Oxide of manganese	trace	trace	trace
Carbonic acid	0·18	0 30	0·48
Siliceous matter	0 40	16·33	0 50
Water and loss	16 45	0·30	17·00

A sample of bleaching powder made from pure lime under the best conditions gave—

Available chlorine	43 13
Chlorine as chloride	9 29
Lime	39 89
Carbon dioxide	0 42
Water	17 00

Preparation of Solution of Bleaching Powder.—Considerable care is

necessary in making the solution to be used for bleaching. In the first place a high temperature of extraction must be avoided, as it causes decomposition. On the other hand, too low a temperature does not favour complete extraction. The solution must be quite free from suspended particles If these be left in they become entangled in the fabrics and cause over-bleaching, *i e.* production of oxycellulose It is obvious that to simply stir the powder with water and let it settle and then draw off the liquor cannot give complete extraction For this some process of decantation and levigation must be adopted The following instructions are due to Messrs Carey and Muspratt, and are the result of considerable experience —

Water - The water used for making the solution should not be cold. The best practical temperature is 75° to 80° F.

Bleaching Powder —The bleaching powder should be emptied into the agitating tank through a 1-inch mesh sieve, the lumps being knocked through with the flat of a spade.

Agitation.—The agitation should be performed so as to show a strong swirl on the surface, say with a periphery speed on the agitator of 500 feet per minute for tanks of 5 to 9 feet diameter, and the lower limbs of the agitator should be no more than 1 inch from the bottom of the tank After completing the volume of the batch, thorough agitation for twenty minutes is ample for all strengths of solution up to 16° Tw Further time spent on agitation is wasted, and by beating up the bleaching powder renders subsequent settling appreciably slower

Clearing Space for Sludge —The run-off pipe should be at such a height as to allow 5 cubic feet of sludge per cwt. of bleaching powder used per batch for all strengths of solution up to 16° Tw. Unless a sufficient space is allowed an enormous waste of time will arise in waiting for the last few inches to settle clear

Washing Sludge —The sludge consists not of bleaching powder, but of insoluble lime suspended in bleach solution When the clear liquor has been run off, the agitating tank should be filled again with water and the contents agitated for five minutes only prior to settling. The clear liquid is then run off, and for all practical purposes one such washing will be sufficient

Efficiency.— When the precautions given above are followed, the loss of bleaching powder in the washed sludge will not exceed 2 lbs per cwt of bleaching powder used, provided the last clear liquor is not more than 2° Tw

If the powder be carelessly extracted it often cakes and forms lumps, which are not afterwards broken down and hence never extracted The powder should be ground before use and first made into a paste with a little water, this paste being afterwards diluted to the required strength.

The Castner-Kellner Alkali Co , Ltd , make the following recommendations —

1 The water used should have a temperature of from 21° to 26° C

2 The liquor should be agitated mechanically and there should be no dead spots in the tank

3 The bleaching powder should be added gradually to a tank which is one-third full of water Lumps should be crushed. After all the bleaching powder has been added, agitation should be continued for twenty minutes The tank should then be filled up with water, agitated for another ten minutes and, finally, allowed to settle.

4 For each 1 cwt of bleaching powder, 5 cubic feet of space must be allowed for sludge and the liquor running-off pipe must be fixed a few inches above the sludge level in order that a clear bleach liquor may be obtained.

5 After running off the clear liquor, the tank should be filled up with water, and again allowed to settle This solution is added to the strong clear liquor and the sludge remaining in the tank is usually dumped

L Griffin (*J S C I*, 1904, p 174), treating of the extraction of bleaching powder, says that when 38 to 39 per cent of available chlorine is present the sludge is of very little consequence and settling is much easier than with lower grades Hence the first condition for rapid and complete extraction is the use of a good powder The quality of the water has an important influence on the results, since it affects the relative specific gravities of the solution and the insoluble matter Thus the presence of even a small amount of carbon dioxide will cause much more rapid settling The temperature of the water is also of importance, since it affects the specific gravity of the solution Within limits a higher temperature induces rapid settling

An important point to decide in making bleaching solutions is what the strength should be Griffin finds that a solution of about 6° to 7° Tw is the most convenient to make From this, together with the liquor from the first washing of the sludge, a solution of about 4 2° Tw is obtained, which gives the best results in practice This is suitable for most purposes and requires a capacity of about 1 cubic foot per 3 75 lbs of a good powder

He recommends the following plant for extraction Two round or square similar concrete tanks of somewhat greater depth than width are provided with agitators and adjustable syphons for drawing off the liquors into a common pipe leading to the storage tank, which should be equal in capacity to the sum of those of the first two The storage tank is at a lower level than the rinsing tanks, so that the liquors flow into it by the action of gravity It is convenient to have the rinsers level with the flow, and better agitation can be obtained with square than with round tanks The extraction is carried out as follows —

A mixture of about 6° to 7° Tw is made up in one tank and allowed to settle, the other containing the sludge from a former extraction of the same strength The latter is filled up with fresh water or a weak liquor, agitated, and allowed to settle After a time the two liquors are drawn off in equal volumes, in equal times, giving a mean strength of about 4° Tw With care a constant strength, which is always desirable for good results, can be in this way obtained The sludge from the second liquor is again agitated with water, thus making a third or weak liquor After settling, this is used to wash the strong sludge from a fresh extraction The residue, after the third extraction, is practically free from chlorine and is rejected, leaving the mixer ready for a fresh charge of powder It would be better to use fresh water for washing the strong sludge and the third liquor for making up the next strong liquor, but this would necessitate the use of four mixers

For large quantities of bleaching powder of about 10 tons daily, four concrete settling tanks, each having a capacity of about 1100 cubic feet, are used These have, as before, adjustable syphons leading into a common conduit The outlet of each syphon is near the bottom of the tank Each is made of 3 inch cast-iron pipe, and is made in the form of an adjustable elbow joint similar to that used in the Archbutt water softener In this way the liquor is drawn off from the surface where it is clearest, and it is not necessary to wait for complete settling The mixing is accomplished in a special mixer by a centrifugal pump, which imparts a rotating motion to the contents of the tank

In working the plant a full settling tank of strong solution is made by discharging the contents of three or four mixers The tank is then allowed to settle

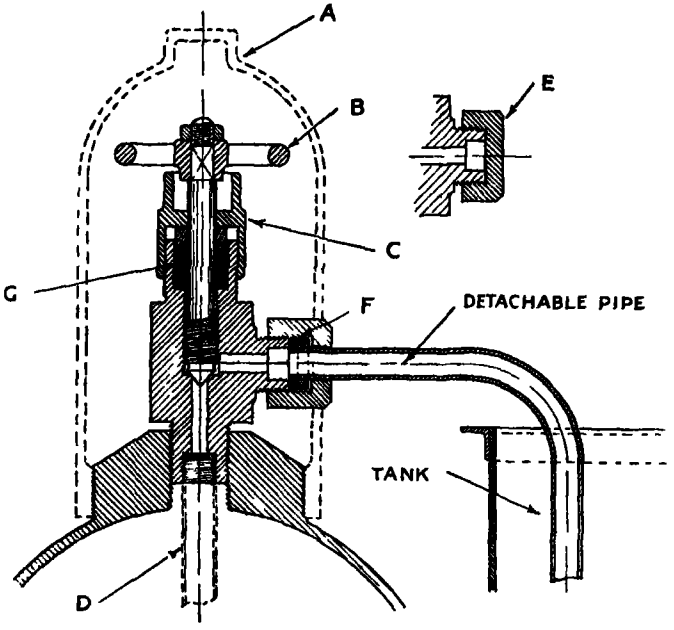
for five or six hours at 55° F, syphoning off the liquor meanwhile. About 3 cubic feet of sludge are left for each 100 lbs. of powder used. The strong sludge is washed twice with water, the resulting liquors being used in subsequent extractions This example is evidently worked out for paper bleaching on a large scale Such large quantities are never required for cotton goods.

The Use of Liquid Chlorine in preparing Bleaching Solutions.—The sludge which is formed when bleaching powder is extracted with water consists as chiefly of free or unchlorinated lime. It is generally thrown away If, however, chlorine gas be passed into the mixing tank while the bleaching powder is being extracted, and is allowed to bubble up through the liquor, this free lime is converted into calcium hypochlorite In this way much stronger bleaching liquors can be obtained, and the quantity of sludge is greatly reduced.

No special plant is required beyond a fairly deep mixing tank and some quarter-inch steam piping to lead the gas into the liquor With such a tank and good agitation, the time necessary for this chlorination does not exceed fifteen or twenty minutes The temperature of the liquor rises slightly during the process, which favours, also, the subsequent settling of the sludge

The Castner-Kellner Alkali Co, Ltd, who manufacture liquid chlorine, claim the following advantages for this method of preparing bleaching solutions.—

1. Stronger liquors are obtained and fewer mixings necessary Since the



UNION CONNECTION

A—VALVE PROTECTING CAP
B—VALVE SPINDLE WHEEL
C—GLAND NUT
D—INTERNAL PIPE FOR LIQUID CHLORINE SUPPLY
E—COVER NUT.
F—DERMATINE OR LEAD JOINT RING.
G—HARD RUBBER AND STEEL WASHERS.

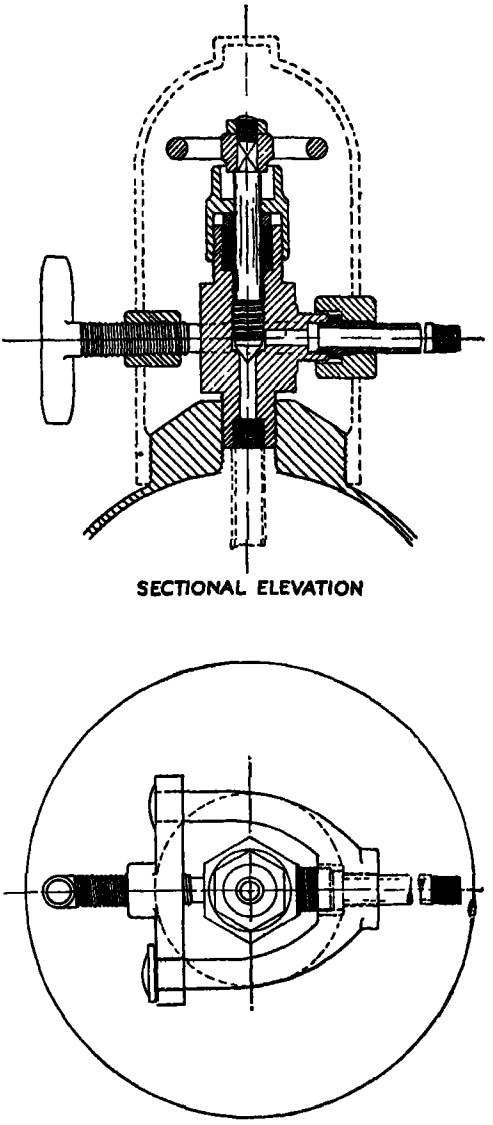


FIG 150.—Chlorine cylinder valves.

liquor is at least 35 per cent. stronger, ten batches will produce as much liquor as thirteen or fourteen do without chlorination. In fact, owing to the small quantity of sludge formed, it is possible to obtain even stronger bleaching liquors and, by using a bigger charge of bleaching powder, and chlorinating it,

to make a strong stock liquor which can be diluted as required. Moreover, owing also to the small amount of sludge, much more of the clear liquor can be drawn off

2 The loss through imperfect solution of the bleaching powder is generally 10 per cent. and may rise to as much as 25 per cent. of the powder used This is avoided by chlorination.

3. The sludge is only about one quarter of that produced when bleaching powder is extracted with water alone The disposal of the sludge is sometimes

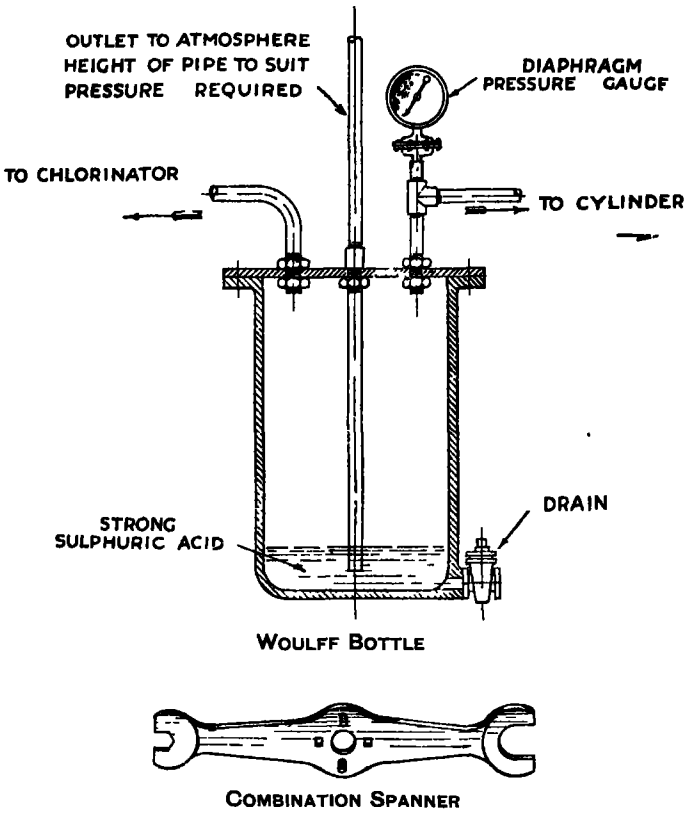


Fig 151.—Woulff bottle.

difficult. Moreover, at least three or four mixings can be made in the same tank without removing the sludge In some cases five successive batches can be made This naturally saves much labour and increases greatly the output of a mixing plant

Liquid chlorine is supplied in cylinders of about 70 lbs capacity When the cylinder is opened the liquid evaporates, yielding chlorine gas The cylinder head and valve are illustrated in fig 150 When not is use, the protecting cap should be screwed down over the valve The outlet valve is protected, also, by a cover nut which should be screwed home. The use of force in opening the

valve must be avoided. A special valve spanner is supplied. In case of difficulty, an iron ring (say a 3-inch coupling ring) should be made black hot and placed over the valve for a minute or two The valve spindle, when made loose, should be kept moving as the valve cools down. In the illustration, the delivery pipe is connected to the cylinder by means of a recessed nut. Another type consists of a stirrup which fits over the valve body A recessed boss holds the collared pipe and a tight joint is made by means of a hand-screw working on the back of the valve The stirrup connection is preferable to the other type, it saves time, wear and tear on the threads of the outlet valve, and does away with the danger of a misfit between the threads of the valve outlets and of the coupling nut. It is advisable to insert a Woulff bottle containing strong sulphuric acid between the cylinder and the chlorinator. This is shown in fig 151

When the consumption of chlorine is very large it may be obtained in tank waggons. A suitable plant for the preparation of bleaching liquors is illustrated in fig 152.

Strength of Solution.—The strength of the bleaching solution varies very much with the nature of the goods and the effect required The exact strength to be used for any particular class of goods is a matter of judgment and experience. Experience has proved that if the preliminary operations are thoroughly carried out, it is possible to bleach completely the most obstinate goods without exceeding a strength of 3 grammes per litre (*i e* about 1° Tw). It is of great importance that the proper strength should be used and maintained, or under- or over-bleaching will result The use of strong solutions should always be avoided, since they invariably tend to cause the production of oxycellulose The concentration to be aimed at is that which will oxidise the colouring matters without attacking the cotton fibre Instead of employing strong solutions, it is better to rebleach with a dilute solution or to employ sodium hypochlorite instead of bleaching powder, since it can be employed in greater concentrations without danger A gradual evolution of the bleaching action is also desirable If the chlorine be too rapidly evolved the goods will not be thoroughly penetrated, while if too slowly they may be damaged owing to the prolonged action of the chlorine The presence of excess of alkali, particularly in the case of sodium hypochlorite, retards the evolution of the chlorine. Thus, incomplete washing after lye boiling increases the time and chemicals necessary for bleaching

The strength of the solution and the temperature at which it is used are very closely connected A solution of bleaching powder increases in activity directly with the temperature Thus, a weak solution at a moderately elevated temperature is often more powerful than a cold but stronger solution Heat must, however, be employed with great care, as it increases the danger of over-bleaching The usual temperature is from 15° to 18° C , but it may be increased with care up to 20° to 25° C , the strength of the solution being correspondingly reduced

Freiberger is a consistent advocate of warm bleach liquors. Thus, he stated (*J Soc Dyers and Col*, 1919, p 201) that solutions of bleaching powder containing 1 gramme of available chlorine per litre, at a temperature of 35° to 37° C for about thirty-five minutes, give good results The penetration is better, the white purer, there is little or no danger of over-bleaching, and the precipitated calcium carbonate is not so troublesome, owing to the fact that it is in a looser and more granular condition

The time necessary for bleaching is reduced greatly. At a strength of 1 gramme per litre of available chlorine a fabric which would require from two

to three hours at atmospheric temperature can be bleached in from ten to fifteen minutes at 35° C

Freiberger's experiments have been criticised on account of the fact that

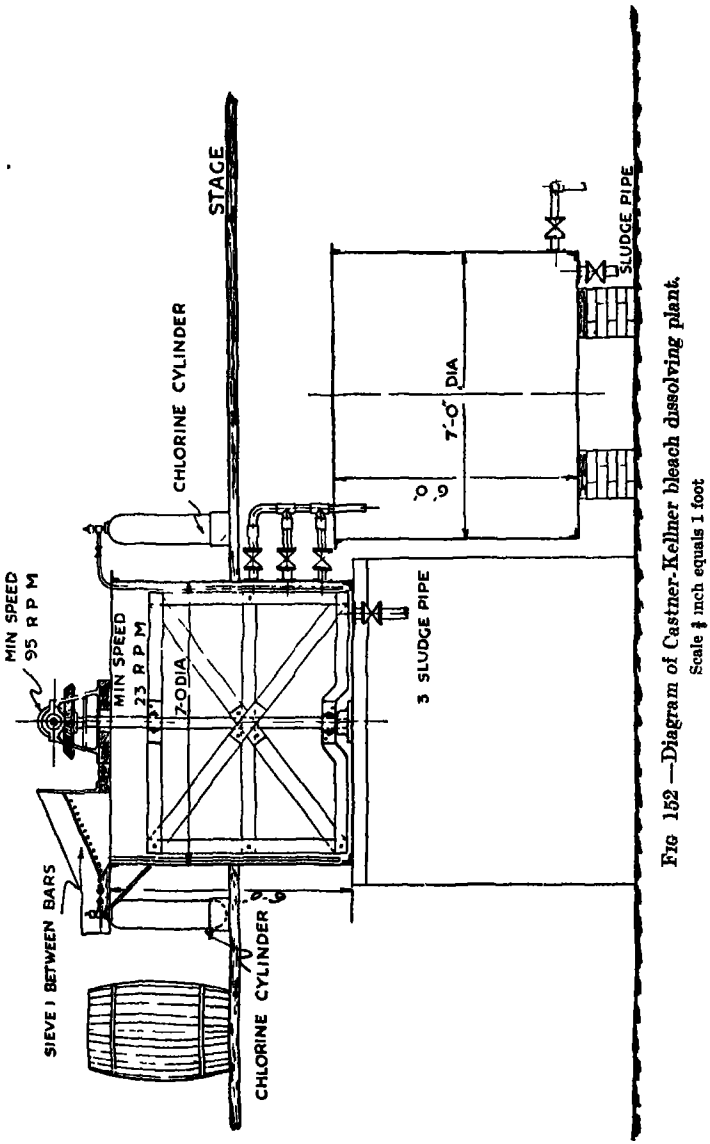


FIG 152.—Diagram of Castner-Kellner bleach dissolving plant.
Scale ½ inch equals 1 foot

only small quantities of material were used, but Trotman and Pentecost (*J.S.C.I.*, 1922, 73T) have used the method on the large scale, though with weaker solutions than those suggested by Freiberger. With bleaching solutions containing 0·5 gramme of available chlorine per litre they found that excellent results were obtained, particularly with sodium hypochlorite.

Checking the Strength of Bleaching Solutions.—The strength of bleaching solutions may be expressed in terms of—

1. The Twaddell hydrometer scale
2. Grammes of available chlorine per litre of liquor, or "grammes per litre."
3. Litres of chlorine gas per litre of liquor, or "chlorometric degrees"

These expressions refer to the methods of testing respectively described below, and their corresponding values for equivalent strengths of bleaching-powder solution are tabulated on p 459

Owing to the variable composition of bleaching-powder solutions, the relations expressed in this table cannot be regarded as applicable in all cases, even of freshly made solutions But as the Twaddell of the liquor has become the usually adopted standard of bleaching strength, irrespective of the inaccuracies associated with the test, it is useful to establish a relation between terms which are proportional to bleaching strengths and those which have become familiarised by usage.

In view of the importance of working with a solution of suitable strength, it is perhaps remarkable that so crude a method of checking as the use of a hydrometer should be employed A solution of bleaching powder contains not only chlorine and hypochlorites, but calcium chloride and lime, all of which may vary in amount While a hydrometer will give approximate results in the case of a solution of a single substance, such as sulphuric acid or caustic soda, it is quite incapable of doing this in the case of a complex solution containing at least four variable constituents. The readings can only be of any value as long as the powder has a constant composition The titration of bleaching liquors should be a matter of routine in every bleaching works, as this yields figures which definitely correspond with the bleaching activity of the liquor and with the progress and cost of a given operation This method affords a ready and accurate indication of the state of a partially exhausted liquor, and what additions are necessary to bring the same up to strength, or whether it is worth while strengthening.

The titration may be carried out by any of the methods described above

The objection which is urged against the testing of chemic by titration is the greater time and care required as compared with the very simple hydrometer test

To meet this objection, the burette may be graduated so as to give direct readings in grammes per litre, or, if preferred, in the equivalent degree Tw The quickest method then becomes the one in which the decinormal solution is placed in the beaker, together with the indicator, as in the arsenious acid process, and the chemic run in from the burette. The burette must be graduated in accordance with the relation—

$$\frac{\text{c c. of decinormal solution} \times 0{\cdot}00355 \times 1000}{\text{c.c. of chemic}} = \text{grammes per litre.}$$

When the scale is specially graduated, it is of course necessary to use in the beaker that number of c.c. of N/10 solution for which the scale is proportioned.

In the corresponding test, in which the decinormal solution is titrated into the chemic, the readings of an ordinary c.c. burette may be made to represent

grammes per litre, by employing that number of c c of chemic in the beaker which fulfils the condition—

$$\frac{1 \text{ c c N/10 sol} \times 0{\cdot}00355 \times 1000}{x \text{ c c of chemic}} = 1 \text{ gramme per litre,}$$

whence $x = 3{\cdot}55$ c c

Many bleachers who realise the inaccuracies of the hydrometer test, but require for practical use a quick and simple test of a fairly reliable character, employ one of the solutions described above, prepared of such a strength that one drop of chemic of known strength will neutralise say 5 c c of the solution and discharge the colour of the indicator The chemic is applied by means of a graduated dropping tube, or by even cruder methods, and the strength of the chemic is calculated as being inversely proportional to the number of drops applied The results are generally expressed in terms of the Twaddell standard

If the chlorine be required in terms of litres and gas per litre of liquor ("chlorometric degrees"), as is sometimes the case, Bottler's process is very useful, since it gives volumes directly

It depends upon the fact that when a solution of chlorine or hypochlorite is treated with hydrogen peroxide, oxygen is liberated The volume of the liberated oxygen is exactly the same as that of the chlorine contained in the liquor This is seen in the equation

$$H_2O_2 + Cl_2 = 2HCl + O_2$$

The test is carried out as follows A nitrometer is filled with water and the side tube connected with a wide mouthed bottle or flask by means of a flexible rubber tube A quantity of hydrogen peroxide solution is placed in the flask, and a measured volume (3 5 c c) of the liquor is placed in a small tube and introduced in such a way that it stands upright, preventing contact between the two solutions The cork is then replaced, thus connecting the flask to the nitrometer The top of the latter is now opened, so that the nitrometer is in communication with the flask The bleaching liquor is next mixed with the peroxide solution by shaking the flask The evolved oxygen is collected in the nitrometer, displacing the water When the evolution of gas has ceased, the free tube of the nitrometer is moved till the level of the water is the same in both, *i e* until the gas is under atmospheric pressure, when the volume is read off The volume is a measure of the active chlorine in the bleaching liquor, and may be easily calculated into litres of chlorine per litre of liquor

As already indicated, the chlorine content of bleach liquors may either be stated as grammes per litre or as chlorometric degrees The latter term denotes the number of litres of chlorine gas present in 1 litre of the liquor Thus, if a bleach liquor has a strength of 1 chlorometric degree, it means that 1 litre contains 1 litre of chlorine gas measured at 0° C and 760 mm pressure In the case of a solid substance, such as bleaching powder, the chlorometric degree refers to 1 kg, *i e* the weight of 1 litre of water Thus, if a given sample of bleaching powder is said to have a chlorometric strength of 100 , it means that 1 kg of the powder is equivalent to 100 litres of chlorine gas measured at 0° C and 760 mm pressure

The gravimetric method of expression is more rational than the volumetric, and is now generally adopted Thus, the strength of bleaching powder is generally returned as a percentage of available chlorine, while the strength of liquors is measured in grammes per litre

CONVERSION TABLE FOR FRESH BLEACHING POWDER SOLUTIONS.

° Tw.	Sp. Gr.	"Grammes per Litre."	"Chlorometric Degree."
0 5	1·0025	1·40	0·45
1·0	1 0050	2·71	0·86
2	1 0100	5 58	1 77
3	1·0150	8 41	2 67
4	1·0200	11 41	3 63
5	1·0250	14 47	4 61
6	1·0300	17 36	5 51
7	1·0350	20 44	6 5
8	1 0400	23 75	7·5
9	1·0450	26 62	8·3
10	1·0500	29 60	9 4
15	1·0750	45 70	14·5
20	1 1000	61 50	19 6
0·3	1 0015	1	0·32
0 72	1·0036	2	0·64
1 1	1 0055	3	0·96
1·5	1 0075	4	1·27
1·8	1·0090	5	1 59
2·2	1 0110	6	1·91
2 5	1·0125	7	2 23
2 9	1·0145	8	2·55
3·1	1 0155	8·5	2 70

The Poncius method (*J S C.I*, 1922, 544A) of estimating available chlorine in bleaching solutions is useful Sodium bicarbonate is added to the solution, which is then titrated with decinormal potassium iodide, using starch solution as indicator, till a blue colour is produced. The iodide is first oxidised to iodate, but as soon as this reaction is complete, the next drop of iodide reacts with the iodate, liberating iodine, which at once gives a blue colour with the starch.

It is necessary sometimes to estimate the alkalinity of a bleaching liquor This is difficult, owing to the bleaching of the indicators used The method of Orton and Jones (*Analyst*, 1909, p 317) gives accurate results The solution to be tested is placed in a Drechsel bubbler and an excess of decinormal acid is added to it The volume of acid necessary to react with the hypochlorite is obtained by titrating the liquor with decinormal thiosulphate. A stream of air, free from dust, is passed through the mixture, in the absence of light, till all the chlorine is evolved. This point can be ascertained by adding one drop of a 0·1 per cent solution of methyl orange. The indicator is bleached if any chlorine is present. When the liquid is free from chlorine the excess of acid is titrated with decinormal sodium carbonate The procedure is the same in the case of solid hypochlorites, except that it is more convenient to introduce the solid into the bubbler before the acid The alkalinity is calculated from the equations

$$Ca(OCl)_2+4HCl=CaCl_2+2H_2O+2Cl_2,$$
$$Ca(OH)_2+2HCl=CaCl_2+2H_2O$$

The thiosulphate or arsenite titre (N/10) of the bleaching solution gives directly the volume of decinormal hydrochloric acid reaction with the hypochlorite.

Free alkali can be estimated, also, by adding a carefully neutralised solution

of hydrogen peroxide until no more oxygen is given off. Methyl orange is then added and the alkali titrated with decinormal acid. If the methyl orange is bleached, it indicates that insufficient hydrogen peroxide has been used

General Conditions of Bleaching.—The apparatus used will be described in the next chapter. The vessels used must be made of wood, slate, or some material which is unattacked by the liquor. The goods, after lye boiling, are washed till quite free from soda, and run into the bleaching tanks through squeezers or rollers to remove excess of water, which would otherwise cause undue dilution of the chemic and hinder penetration It is very important to remove all the alkali, since, if present, it will render the chemic more strongly alkaline, and therefore less sensitive, this would retard the bleaching action Absorption of chlorine proceeds rapidly at first, but soon ceases, after which it is useless to leave the goods longer in the bath The rate of absorption should be tested from time to time by one of the methods described above As long as bleaching action is taking place the chlorometric strength of the liquor will fall. According to Tailfer, no absorption of chlorine occurs after three hours But this, and also the total quantity of chlorine which disappears, depends largely upon the nature of the goods and the thoroughness of the preliminary processes. In all cases the curve of absorption rises very rapidly at first, but becomes gradually flatter (fig 148A) In bleaching, as carried out by the usual methods, the concentration of the bleaching liquor falls from the beginning to the end of the operation According to a recent German patent better results are obtained if this is reversed, *i e* if a solution of gradually increasing concentration is used. This is said to give a better colour and to be accompanied by less danger of over-bleaching

The proper strength of a bleaching solution is the least which will bleach the residual colouring matters without producing oxycellulose. Heermann and Frederking (*J S C I*, 1922, 54A) drew attention to the danger of using bleaching liquors at too great a concentration They found that the decrease in the tensile strength of cotton fabrics during bleaching increases directly with the concentration of the liquor used. When the latter was doubled the former was trebled Liquors of a concentration of 2 grammes of chlorine per litre caused also a decrease in elasticity.

The usual practice is to bleach in an alkaline liquor in order to control the action Acid liquors are generally considered dangerous. But Ristenpart (*J S C.I.*, 1922, 809A) makes the rather striking statement that this idea is fallacious According to him, better whites and less oxycellulose are obtained by first treating the goods with an acid bleaching liquor of sp. gr. 1·007, containing 2·5 c c. of sulphuric acid per 500 c c of liquor, and then washing and treating with an alkaline bleaching liquor

Schwalbe and Wenzl (*J S.C I*, 1923, 50A, 711A, and 924A) observed that in the case of wood pulp there is a distinct advantage in bleaching at a temperature of from 30° to 35° C, while passing a current of air through the bleaching liquor shortened the time necessary for bleaching by one-half. They state that in the action of hypochlorites on all types of cellulose there is a continuous formation of carbon dioxide amounting to from 0·26 to 0·28 gramme for each gramme of chlorine consumed by 100 grammes of cellulose. When this carbon dioxide is not removed it combines with the calcium hydroxide present, forming calcium bicarbonate, which acts as a buffer and ultimately brings the bleaching process to an end The favourable influence of a current of air is purely mechanical It acts by helping to carry off the carbon dioxide. Similar results were obtained in the total absence of air by a current of pure nitrogen. The carbon dioxide

mentioned above is supposed to be formed by the oxidation of organic matter by the bleaching powder Waentig (*J.S.C.I.*, 1924, 291B), however, criticises these statements, pointing out that there is little reason for supposing that the accumulation of carbon dioxide would inhibit bleaching action

But the matter is a suitable one for further experiments. The experiments of Schwalbe and Wenzl are quite opposed to the common experience that old bleaching liquors are more active than fresh ones. Spent liquors are frequently strengthened for the next lot of goods. The increased activity of old liquors is counter-balanced by the large amount of organic matter frequently held in solution, and occasionally by the possibility of the presence of soluble chloramines (p 50). The reason why old liquors are more active than fresh ones is not quite clear. They contain much calcium chloride, and it is possible in the light of the researches of Taylor and von Tiesenholt that this has something to do with their activity. When more bleaching-powder solution is added to an old liquor the excess of calcium chloride would cause the reversion of the equation

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O,$$

and this produces an immediate stimulation of the bleaching action of the mixture

Higgins has shown that the presence of calcium chloride increases the attraction of the solution for atmospheric carbon dioxide, and this may be a contributory factor. But he noted, also, that old chemics give a precipitate with lime water The precipitate consists of calcium oxide combined with organic matter. Hence, when an old liquor is mixed with a fresh one, organic matter is precipitated, carrying down with it some of the dissolved calcium hydroxide. This reduces the concentration of the solution with respect to calcium hydroxide and upsets the equilibrium of the equation

$$Ca(OCl)+2H_2O \rightleftharpoons 2HOCl+Ca(OH)_2,$$

and this causes the liberation of hypochlorous acid or chlorine.

The practical significance of these considerations is very evident in the difficulty with which the bleaching activity of an old liquor can be controlled in the treatment of goods in which the colour of a dyed portion has to be preserved. The difficulty and risk of damage is not less in the case of white goods, but the effect may be less easy to detect

The use of capillarising agents in the bleaching-bath may be referred to. Thus, in the patent process of Pratt and Arban, the addition of castor-oil soap or turkey-red oil is recommended It is claimed that, owing to the strong capillary action (or wetting power) of these bodies, the liquor is able to penetrate the fibre very rapidly, and perfect bleaching is effected without the intervention of the lye boil and at ordinary temperatures. The process appears, however, to be chiefly adapted to cotton-wool, yarn, and materials whose fibres are easy to penetrate. The following is a summary of the advantages of the method given by the authors, and an example of the bath used.

The advantages claimed over the old bleaching processes are—

1 Suppression of boiling or steaming, saving in apparatus, steam, materials, time, and labour

2. Avoiding the faults caused by boiling.

3. The fibre is less affected ; there is no coating or over-boiling, no roughening, and only a small loss in weight.

An example of a suitable treatment and proportions of materials is as follows —

One hundred kgs of raw cotton, for instance, in the shape of cops, are impregnated with 500 litres of a solution of hypochlorite of soda with 0·3 per cent of effective chlorine, with the addition of 10 litres of turkey-red oil of 75 to 80 per cent (or castor oil soap), and washed out after about two to three hours

Higgins (*J S C I*, 1914, p 902), who made a critical examination of this process, found that about five times as much chlorine was required as compared with the ordinary methods

After chemicking, goods should never be left lying in contact with the chemic, but should be immediately washed in water and soured On standing in contact with even dilute solutions of hypochlorites, cotton becomes changed into oxycellulose, which, when dried or hot calendered, gives rise to tendering or yellowish stains

Philip (*J S C I*, 1901, p 358) has recorded the following illustration of this Cotton goods were noticed to develop yellow or brownish stains after hot calendering, when bleached in a new factory The essential difference in procedure was that the goods coming from the chemic were stored in piles, and exposed to the air for some time Subsequent investigation showed the discolorations to be due to oxycellulose, and the trouble disappeared with the exposure to air and consequent evaporation was prevented This formation of oxycellulose seems to indicate that bleaching by exposure to air, in order to make use of atmospheric carbon dioxide, is attended with danger

CHAPTER XXIV.

SOURING.

The Bleaching Process and the Apparatus used.—The bleaching process is comparatively simple The diluted bleaching-powder solution (or chemic) is placed in a suitable vessel and the goods are worked in the liquor till they are sufficiently bleached, suitable aeration being provided for

The washed goods are run into the bleaching-tank through squeezers or rollers to remove excess of water, which would cause dilution of the bleaching liquor and delay penetration of the goods The common method is to pass the fabric from the washing machine, giving it a final nip to squeeze out as much water as possible, into the chemicking vessel by overhead winces Fabrics which are, for any reason, difficult to penetrate are impregnated with the chemic in a washing machine before passing them into the bleaching-tank

For the efficient working of the bleaching operation the following conditions must be observed —

1 Thorough impregnation of the fabric
2 Uniform distribution of the liquor
3 Control of the strength of the liquor and its temperature.
4 A proper degree of aeration

The fulfilment of the first condition is assisted, as mentioned above, by mechanical impregnation, but is dependent primarily upon the completeness of the lye boil An important function of this process is to render the goods perfectly permeable to the bleaching liquor. Unremoved oil or wax, the presence of calcium or magnesium soaps deposited during the process, residual pectoses or proteins, all inhibit permeability and make bleaching difficult The uniform distribution of the liquor may be assured by circulating either the chemic or the goods, and aeration is provided for at the same time.

The chemic tank consists of a square vessel of wood or stone (fig. 153), the sides braced together by plates and tightening bolts.

In the vessel are two orifices fitted with plugs, and delivering into the waste drain and chemic well respectively The plugs are tapered to fit the orifices, and extend vertically through troughs to enable them to be raised or lowered without impediment from the fabric in the tank They may be secured when raised by a locking pin passing through the shank and resting on the side of the tank A false bottom in the tank supports the fabric, assisting drainage

The chemic well, of stone or cemented brickwork, lies beneath the tank and communicates with it by a circulating pump which delivers the liquor to a perforated trough or troughs resting loosely on the top of the tank. These are shaped to spray the liquor evenly over the surface of the fabric

The accompanying aeration of the chloride of lime increases its activity, while a further aeration of the fabric occurs during draining. It may also be reeled

from one tank to another for this purpose, and to equalise the treatment imparted throughout its length.

The chemic well serves to prepare the chemic at a convenient degree of dilution and maintain the strength as it becomes exhausted. This is done by additions of small quantities of stronger liquor from a carboy or supply pipe connected with the storage tank containing the supply of strong liquor.

The chemic is generally used over again for treating the next batch of fabric, being diluted or strengthened, as necessary, by addition of water or bleaching liquor A certain amount is always lost by absorption or incomplete draining.

Iron is sometimes used for the pump and pipework where chloride of lime is used, as this soon deposits a protective coating of carbonate of lime, but this

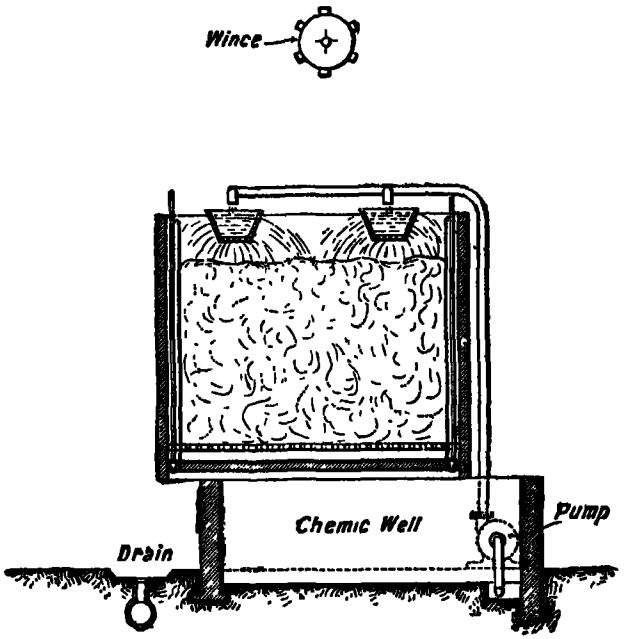


FIG. 153.—Bleaching-tank.

ultimately chokes up the pipes. Lead, phosphor-bronze, or vulcanite are to be preferred Iron must not be used in the souring system

The starting or "priming" of the centrifugal pumps sometimes gives trouble. This is avoided by fixing the pump low enough to be charged by gravitation of the liquor Attention to such details as extreme length of gland bearing, and ring lubrication of the outer one, accessibility for inspection and repairs, goes far to reduce inconvenient and serious stoppages. It is better to fix the striking gear on the overhead counter-shaft than to use two pulleys on the pump, since this saves unnecessary wear.

It is advisable to have a series of such bleaching units, so that different batches can be treated independently at the same time.

It is sometimes convenient to chemic through the machine and merely pile on stillages, but this method has little to recommend it beyond liberation of chemic tanks for other work. It is employed when the fabric is too heavy for

impregnation by circulation, and is thought to give a better chance for aeration. This method, however, demands excessive initial strength of chemic and lends itself to over-bleaching Further, the atmospheric effect is applied too much to the outer layers of the batch, and the general result is liability to irregularity and local production of oxycellulose

It is impossible to obtain quite the same uniformity of impregnation when the liquor has to be applied in the machine as when it is circulated, as described above, since the maintenance of a definite strength of liquor in the machine is a matter of some difficulty The better method is to reel from tank to tank, maintaining the desired strength in the tank, and if a squeeze be necessary, employ the machine for this purpose

A squeezing machine placed between two tanks to perform this operation is called a jigger

The bleaching and souring systems should always be kept separate, the reagents used in the respective cases must not be allowed to come together

Circulation by compression and exhaustion is mentioned in Chapter XVIII in relation to the scouring of cops, cheeses, warps on beam, and loose and raw cotton, and the same treatment applies to their bleaching and souring

Bleaching cloth in the open width is effected by the apparatus described in connection with the Jackson system, in the chapter on Kiers

In the treatment of goods which cannot for any reason be handled in the rope form, it is sometimes sufficient to bleach by steeping in an open chemic tank considerably shallower than the apparatus described This is particularly applicable to the bleaching of lace goods in the bundle form

The chemic is brought to a suitable strength in a tank of about 3 feet depth and of convenient capacity The bundles are dried in a hydro extractor and plunged into the chemic tank and allowed to float loosely When sufficiently bleached they are withdrawn individually and washed in the dollying machine, and soured in the same machine or else transferred to a sour tank

Separate tanks are used for the grey and white chemic and sours

A better method consists in the use of cages or receptacles of wood with perforated sides and bottom These are charged with material to be bleached, and dipped bodily into a chemicking tank by means of a rope and pulley The cage is subsequently lifted out of the tank and allowed to drain into the tank, after which it is removed and washed and soured in the same cage

A very effective method of chemicking or souring is that employed in "vacuum kiers," of which there are several varieties

In the simplest one now in operation (and used for chemicking raw cotton without scouring, for the manufacture of merino), an iron kier (fig 154) with removable but hermetically sealed lid is internally lined with glazed bricks A lead pipe connects the base of the kier with the chemic well Towards the top of the kier is another lead pipe which communicates with an air-exhausting pump It also contains a glazed inspection chamber and a relief valve to break the vacuum The kier is tightly packed with the raw cotton, which rests on a perforated grid, with an attachment enabling it to be elevated to discharge cotton after bleaching

When the kier is packed and sealed, the vacuum is applied, exhausting the air from the cotton, rendering it readily absorbent of the liquor, which is drawn up from the well until it enters the inspection chamber The relief valve is then opened and the vacuum destroyed

The chemic returns by gravity to the well, meanwhile drawing air through the cotton, which, owing to the presence of atmospheric carbon dioxide, assists

the action of the chemic This process is repeated three times, or until the required degree of bleaching is produced.

Experiments made by the authors with such a plant have proved that better results are obtained by using sodium hypochlorite than chloride of lime, there was consequently a discontinuance of the use of the latter

Another form of vacuum kier employed especially for the bleaching and souring of yarn and cops is illustrated in fig 155, and has the advantage of effecting continuous circulation. The figure shows the connections to the chemic well only, but a similar well lies alongside, and duplicates of valves F and R and their down pipes connect with the same.

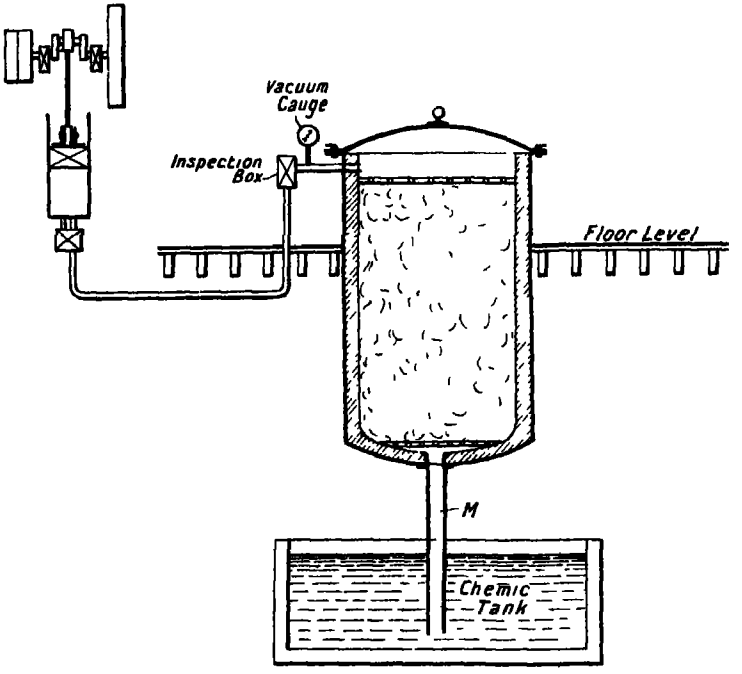


FIG 154.—Vacuum apparatus for raw cotton

F and R are rubber-seated valves with weighted levers which can be raised or lowered to operate the valves E is connected to the vacuum pump W is a water-supply valve for rinsing the kier, and D is the waste effluent valve for draining away the washing water I is an air injector for circulating the liquor Air enters through the inlet A either at atmospheric pressure or under compression

The kier may be filled by suction either through F or R R also serves to return the chemic to the well after bleaching.

When the kier has been charged with liquor, E being still opened to the exhaust pump (not shown), the regulating handle of the injector is turned to admit air at A, and the liquor is circulated through it from the return, to the delivery pipe, and thus through the kier The air is exhausted at E, whereby the atmospheric pressure serves to effect circulation in either direction.

All the above appliances are suitable for either chemicking or souring. The

processes are, of course, separated by a thorough wash. In the case of yarn and loose goods this is carried out *in situ*, especially if a readily soluble bleaching agent, like sodium hypochlorite, has been used

The bleaching vessel illustrated in fig 156 by the Calico Printers' Association

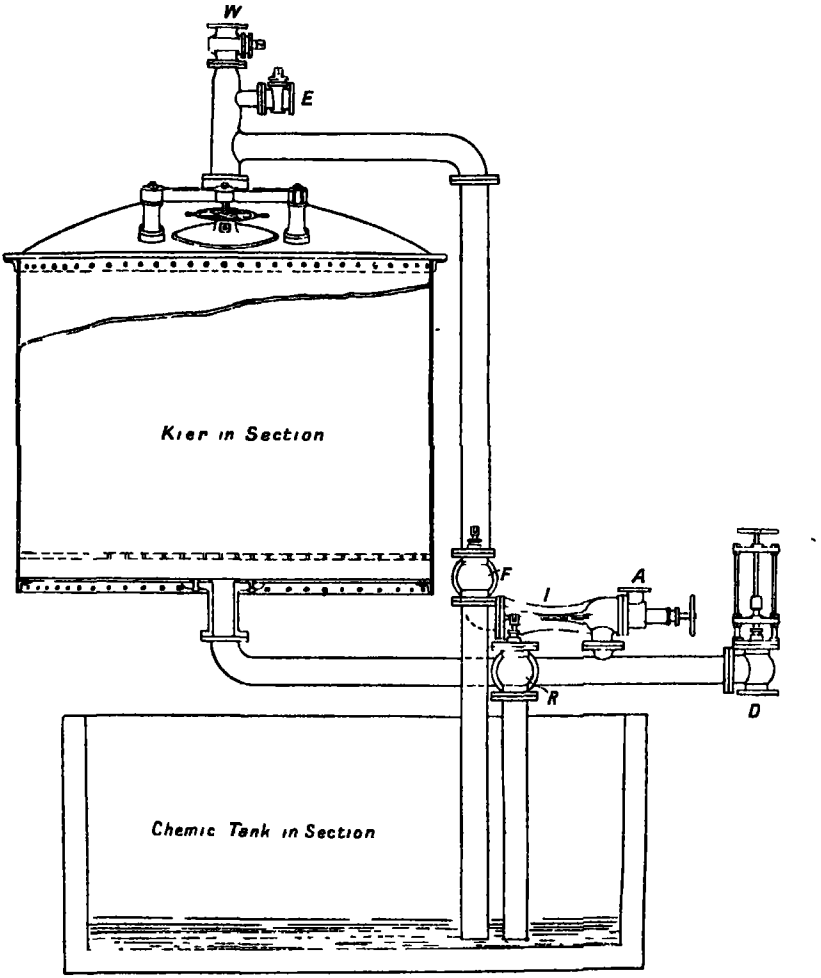


FIG 155.—Vacuum kier

and F Roberts (*J. Soc Dyers and Col*, 1919, p 195) is suitable for the treatment of fabrics in the open width

The figure is a sectional elevation of the machine. The vessel (*a*) is fitted with a false bottom (*f*) of glazed earthenware slabs, and inside this is a removable frame (*g*), the bottom of which may be either of wood or formed of rollers (g^2). The space between the frame (*g*) and false bottom (*f*) is such that the passage of the cloth through the machine may be easy. The fabric (*x*) is pleated down into the vessel, and is led through the same to one of the pairs of rollers

(i, i^1, or j, j^1). The liquid enters the inlet (b), and is drawn through the outlet (d) by means of a suction pump

When the bleaching is completed the goods are immediately washed with water to remove the chemic. They should never be left lying about in contact with unremoved liquor, since this is likely to cause over-bleaching, especially at the outside, where the liquor can become concentrated by evaporation of water.

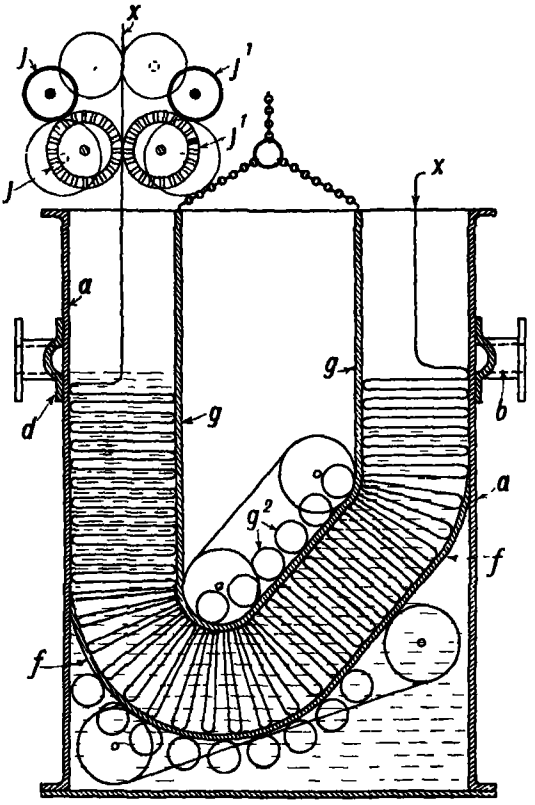


FIG 156.—Bleaching vessel

As soon as they have been washed the goods are "soured," *i e* treated with a dilute solution of sulphuric or hydrochloric acid

Souring.

It has been mentioned before that calcium carbonate is formed during the bleaching process Much of this is deposited on the goods, and is not removed by washing with water If it be allowed to remain, the goods have a harsh feel when dried. The primary object of the "sour" is to change this calcium carbonate into a soluble salt, such as sulphate or chloride, which can be removed completely by washing with water—

$$CaCO_3+H_2SO_4=CaSO_4+CO_2+H_2O,$$
$$CaCO_3+2HCl=CaCl_2+CO_2+H_2O.$$

It must be noted very carefully that acids are not used to complete the bleaching by decomposing calcium hypochlorite left in the goods. If the washing, after chemicking, has been carried out efficiently, only traces of chemic will be left If the washing be incomplete and much calcium hypochlorite remains, over-bleaching is likely to result when the goods are soured. This is because, in the presence of excess of acid, there is an immediate evolution of hypochlorous acid and chlorine. Bleached cotton generally does develop a slight smell of chlorine when soured, but this is due simply to traces of the bleaching-powder solution which are not washed out completely by water. It may be said, therefore, that the acid helps to clear the goods from traces of calcium hypochlorite not removed by the previous washing, but this is a secondary consideration. The main point is not to finish the bleaching in the acid-bath, but to use it for its legitimate purpose. This point is not always realised by students.

The strength of the acid-bath is from 1° to 2° Tw. and the temperature that of the atmosphere. The apparatus used is the same as for the chemic. The sour is prepared in the well by adding acid in small quantities to the water, the mixture being well stirred to prevent the heavy acid from accumulating at the bottom of the tank which, of course, must be made of wood or stone.

Either the acid or goods must be kept in motion, to ensure that every portion of the latter is acted on From half an hour to an hour is required for complete penetration of the acid, depending upon the nature of the goods. When dealing with heavy goods it is permissible to raise the temperature slightly. As long as the goods are kept completely covered there is no danger of causing tendering It must not be forgotten that raising the temperature produces practically the same effect as increasing the concentration of a cold sour. Hydrochloric acid removes calcium carbonate more readily than sulphuric acid, on account of the greater solubility of its calcium salt But in practice, for reasons of economy, sulphuric acid is always used. During the war, nitre cake, or crude sodium-hydrogen sulphate, was employed for souring It contains from 17 to 35 per cent of available sulphuric acid

After souring, the goods must be immediately washed with water till every trace of acid has been removed The destructive effects of sulphuric and hydrochloric acids upon cotton have been described in Chapter IX Failure to wash out acid completely, after souring, is one of the commonest faults in cotton bleaching. A dilute cold bath of sodium carbonate or ammonium carbonate may sometimes be introduced during the washing, especially in the case of goods which are to be finally soaped.

Repetition of Processes.—Some, or all, of the operations which have been described are often repeated when the goods are difficult to deal with, or the highest degree of purity is required The repetition of comparatively mild processes is less likely to cause physical or chemical alteration of the cellulose than one application of a more drastic treatment Hence, bleaching is not always so simple to carry out as it may appear from the foregoing pages. These "repetitions" will be dealt with in Chapter XXVII, in which "processes" are described

The Analysis of Bleached Cotton.—It will be convenient to recapitulate and extend the tests already described for the analysis of cotton, with special reference to the requirements of bleached goods A general analysis should include the following qualitative and quantitative tests :—

1. *Freedom from Acid.*—Acid is detected by means of methyl red (p. 133).

2. *Freedom from Chlorine, Hypochlorites, or Chloramines.*—No bleached cotton should liberate iodine from an acidified solution of potassium iodide.

If it does, it may contain either adsorbed chlorine, hypochlorites, or chloramines. The two former are decomposed, when treated with an acidified solution of hydrogen peroxide, while chloramines are not. If, after this treatment, the cotton be washed with water, treated carefully with a very dilute solution of potassium permanganate to decompose any residual hydrogen peroxide, and again washed, only chloramines can remain, which will still liberate iodine from an acid solution of potassium iodide

3. *Ash* —This is determined in the usual manner. In a well-bleached sample the ash does not exceed 0·1 per cent If higher, the calcium should be estimated. Imperfect souring and washing leaves a residue of calcium salts which may cause harshness Iron would be indicated by its colour The ash of a bleached cotton should be white or grey in colour

4. *Oil and Wax.*—Only traces of these should be present. The estimation is made by means of a Soxhlet or continuous extractor, as described on p 76 Residual cotton waxes are the commonest cause of trouble

5. *Total Nitrogen*—This is determined by the Kjeldahl process described on p 56

6 *Copper Number* —The methods used for the determination of the copper number have been discussed in describing oxycellulose (p 113). Well-bleached cotton should have a low copper number (0·3 to 0·5).

7 *Matter Soluble in Sodium Hydroxide.*—About 5 grammes of the sample are dried, weighed in a stoppered weighing bottle, and boiled for from two to three hours in a flask containing about 500 c c of 2 per cent sodium-hydroxide solution, a reflux condenser being used The boiled cotton is washed thoroughly with hot distilled water, soaked in a 1 per cent solution of acetic acid and again washed with water. It is then dried and weighed in the weighing bottle Incompletely boiled cotton may lose up to 5 or 6 per cent, but if well scoured and not over-bleached the loss is very small.

Birtwell, Clibbens, and Ridge (*J Text Inst*, 1925, T 21) use this test as a substitute for the copper number if the material has not been boiled with alkali already Their method of carrying it out is as follows About 2 grammes of the material, dried at 110° C., are weighed and boiled with 200 c.c of a 1 per cent. sodium-hydroxide solution for four hours in a flask provided with a reflux condenser The liquid is then poured off through a weighed Gooch crucible, and the residue washed successively with a 1 per cent sodium-hydroxide solution, water, N/10 sulphuric acid, and finally with water till the washings are neutral The crucible and its contents are then dried at 110° C. and weighed

8 *Methylene Blue Test* – This has been referred to already in Chapter VIII as a means of detecting oxycellulose It has been investigated fully by Constance Birtwell, Clibbens, and Ridge (*J Text Inst*, 1923, T 297). The method of testing employed was as follows From 1·5 to 2 grammes of cotton, cut into small pieces, were shaken for eighteen hours in a glass-stoppered bottle, at room temperature, with 50 c c. of a solution of methylene-blue hydrochloride containing approximately 0·4 millimole per litre. Some of the solution was then withdrawn and its concentration determined by comparison, in a colorimeter, with a standard solution of methylene-blue hydrochloride containing 0·2 millimole per litre.

Carefully bleached cotton, which approaches pure cellulose very closely, absorbs small but definite quantities of methylene blue. Unbleached cotton absorbs much more than bleached cotton owing to the presence of proteins and other impurities. The progressive elimination of these impurities should be accompanied, therefore, by a gradual decrease in the adsorption of methylene

blue by the cotton. The method of determination of methylene blue used was that described by Pelet-Jolivet, namely, titration with naphthol yellow S. When a solution of this dyestuff is run into one of methylene blue, a reddish-brown precipitate is formed, the blue colour of the solution becomes less intense, and finally yellow when the reaction is complete. The end point is difficult to see, since the precipitate does not settle rapidly. This difficulty was overcome by titrating the methylene-blue solution in a thick-walled, flat-bottomed tube of about 50 c.c. capacity which fitted the brass buckets of a centrifuge.

The following conclusions were reached by these authors —

1. For cotton of known origin, the methylene-blue absorption offers a method of following quantitatively the progressive purification of cotton cellulose during bleaching, and, ultimately, of measuring the success of the bleaching process.

2. For a known bleaching process, the absorption of the bleached material gives information on the origin of the raw cotton, distinguishing sharply, for example, between Egyptian and American cottons

In using the test to indicate over-bleaching certain factors must be considered, *e g*

(*a*) The ash content, or, more strictly, ash alkalinity, affects the absorption. The ash alkalinity is controlled chiefly by the nature and efficiency of the washing processes

(*b*) The origin of the raw material is an important factor Whilst American cottons, bleached by a normal and efficient process, all show the same absorption within narrow limits, the Egyptian cottons when bleached by the same process show higher absorptions, varying with the type.

(*c*) When the quality of the cotton remains the same, the absorption is determined by the efficiency of the bleaching operations In particular, if the scouring process insufficiently removes the non-cellulose impurities of the raw material, a high absorption results, which is not corrected by the subsequent chemic.

(*d*) The addition of soap or olein to the kier liquor results in an increased absorption of methylene blue by the bleached material when these substances are left on the cotton, for example, in the form of insoluble soaps.

(*e*) Processes, such as calendering and mercerising, which alter the surface properties or degree of dispersion of cotton cellulose, have no effect on the absorption

In a later paper (*J Text. Inst*, 1925, T 13) the same authors give detailed results of investigations into the suitability of the methylene blue and other tests for the analysis of bleached cotton. Two types of oxycellulose are distinguished, one characterised by great affinity for methylene blue and abnormal retentive power for alkalis; the other by high reducing power (as expressed by the copper number) and excessive loss in weight on scouring

If the cotton has been so affected by oxidising agents that the second type of oxycellulose has been produced, it regains its original chemical properties on scouring with alkali, though, of course, suffering loss in weight A determination of the copper number will not, therefore, detect this kind of damage if the material has been scoured after bleaching. The measurement of the viscosity of a solution of the cotton in " cuprammonium " does, however, reveal changes in the cellulose, no matter what the conditions of oxidation or the subsequent treatment may have been On the other hand, other changes, besides those caused by oxidising agents, may bring about the same reduction in viscosity, but this is not likely to happen as the result of a normal alkali scour. The copper number is recommended as a useful criterion of the

permanency of white in bleached cotton, the methylene-blue absorption as an indication of level dyeing properties, and the viscosity as a means of detecting tendering in a normal process of scouring and bleaching Which type of oxycellulose is produced predominantly in a given bleach depends chiefly upon the acidity or alkalinity of the hypochlorite solution. On the alkaline side of the neutral point the product has a high methylene-blue absorption and low copper number, but on the acid side the absorption is low and the copper number high.

Other tests of importance are—

Liability to Yellow.—This may be tested by steaming the sample for half an hour in an autoclave at about 1 atmosphere pressure. Freiberger moistens the cotton with a solution of sodium ricinoleate and steams at ordinary pressure.

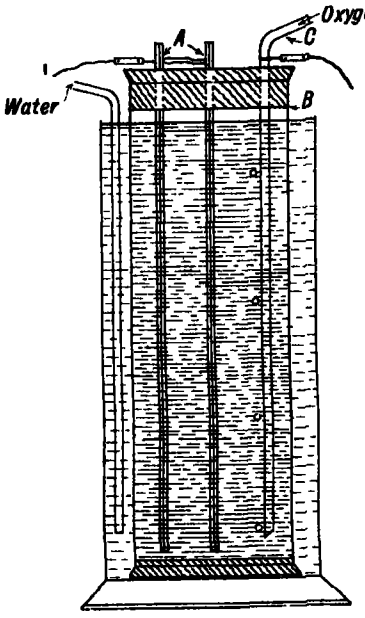


Fig 157.—Cuprammonium apparatus

Wood Gum Value.—Piest (*J.S.C.I.*, 1913, p 17) describes this as the percentage of matter soluble in a cold 5 per cent solution of sodium hydroxide after prolonged standing. It is a complex function including small quantities of fatty acids, gum, and the soluble products of overbleaching (*i e* alkali soluble oxycellulose) Normally bleached cotton gives a value of from 0·5 to 1 per cent.

The hydrate copper value (Piest) is the percentage of cupric oxide absorbed from cold Fehling solution This is regarded as indicating the state of hydration of the cellulose, being specially pronounced in the case of mercerised cotton, normal (0·5) in the case of oxycellulose, and particularly low for hydrocellulose

The Acid Value.—This is the amount of sodium hydroxide neutralised on boiling for half an hour with a 1 per cent solution This is a complex function, indicating primarily the chemical modification due to oxycellulose and hydrocellulose in approximately equal degrees, and, secondarily, the specific susceptibility of the cellulose itself to alkaline hydrolysis. It is particularly low in the case of cellulose which has been treated already with strong alkali (*e g.* mercerised cotton), and which is not otherwise modified by drastic oxidising or acid treatment which would increase the tendency to hydrolysis.

Osts Viscosity Test.—This is a valuable measure of chemical condition The cotton is dissolved in cuprammonium solution and the viscosity of the solution is determined. The viscosity is closely related to the treatment to which the cotton has been subjected. This test has been studied critically by Farrow and Neale (*J. Text. Inst*, 1924, T. 157). The following details are taken from their paper They conclude that although definite values cannot be established for the viscosity of cotton at any normal stage of manufacture, comparisons of the viscosities of a given material, before and after treatment, afford an extremely sensitive indication of the inception of structural changes in the cellulose. For example, kier boiling, especially if air be present, causes a fall in viscosity, as does boiling in extremely dilute acids. The process is

thus well suited for the control of the various bleaching operations. The following cuprammonium solvent is recommended It contains 14·8 to 15·0 grammes of copper and 236 to 245 grammes of ammonia (NH_3) per litre It is prepared by electrolysing strong ammonia solution in a tall glass cylinder (B, fig. 157), using copper electrodes (A and C) with a current density of 0·02 amp. per cm^2.

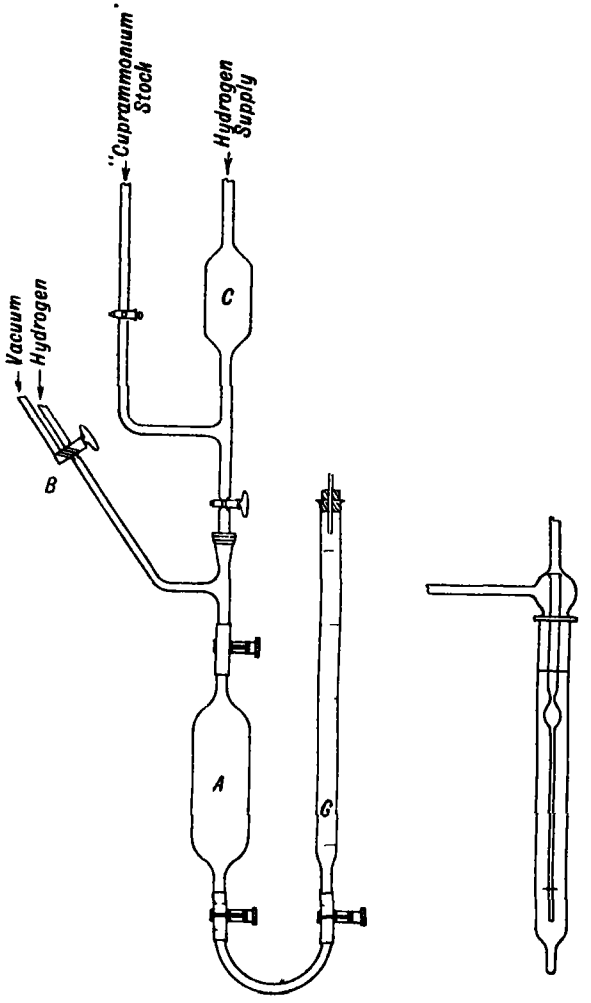


FIG. 158.—Viscometer

The cathode consists of copper tubing through which oxygen is led to the bottom of the cylinder and made to bubble slowly through the liquid. The whole is cooled by circulating water in a jacket One gramme of cane sugar is added to each litre of ammonia solution before the electrolysis begins in order to prevent the disposition of cupric oxide at high concentration. After twenty-four hours the solution should contain about 15 grammes of copper per litre. A certain amount of nitrite is formed, but should not exceed 2 grammes per litre,

calculated as nitrous acid The copper is estimated by titration with potassium iodide and standard thiosulphate, and the ammonia by titration with normal sulphuric acid, using methyl red as indicator, allowance being made for the copper present Nitrite may be estimated by determining the amount of cuprammonium solution necessary to decolorise 10 c c of 0·1N permanganate in the presence of excess of dilute sulphuric acid Adjustment to any desired concentration may be effected by adding the calculated quantities of distilled water or ammonia solution, or by passing in ammonia gas. The solution is stored in a blackened aspirator bottle connected to hydrogen in order to exclude light and air, the side tube of the measuring pipette (C, fig 158) is fitted into the lower hole of the bottle It is advisable to stir the solution from time to time by means of a current of hydrogen in order to equalise concentration

Method of Experiment —The moisture content of the cotton having been determined, a weighed quantity is introduced into the bulb A, which is connected up as illustrated, and alternately evacuated and filled with hydrogen by manipulating the three-way tap B Fifty c c of cuprammonium solution are then run into A from the measuring pipette, after which A is filled with hydrogen, closed and disconnected The bulbs are shaken till solution is complete The bulb is then connected to the viscometer by means of a U-bend and rubber tubing, and the liquid driven out by means of hydrogen. For a 2 per cent solution the falling sphere viscometer is recommended. This is shown in fig 158 It consists of a tube, G, 1 cm in diameter, with five etched rings at 5 cm intervals. The tube is held vertically in a thermostat, a $\frac{1}{16}$-inch steel ball is dropped down the axis of the tube, and the time it takes to traverse the last 15 cm is noted. The tubes are calibrated with castor oil of known viscosity and the constant obtained. In the viscometer of Farrow and Neale this varied from 0·404 to 0 412 That is, the time of fall in seconds of a steel ball $\frac{1}{16}$-inch in diameter through 15 cm multiplied by this factor gives the viscosity of the solution tested in C G S units The authors concluded that the viscosity of a 2 per cent solution responded very delicately to small variations in the treatment applied to the cloth As a general rule over-treatment at any stage causes low viscosities, and it is suggested that measurements of the viscosity of samples taken at each stage would give the bleacher a means of controlling the extent to which the goods are attacked by the chemical treatments he employs. Many other details are given in the original paper, which should be consulted

CHAPTER XXV

SODIUM HYPOCHLORITE, CHLOROUS ACID, CHLORIC ACID, PERCHLORIC ACID.

Sodium Hypochlorite, NaOCl.

Solutions of sodium hypochlorite are used frequently instead of bleaching powder They have advantages in the case of fine goods Sodium hypochlorite is readily soluble in water, and can be washed away with water more completely than a solution of bleaching powder. It does not produce any insoluble by-product, and there is less danger of harshness in the finished goods When it is hydrolysed by water, sodium hydroxide and hypochlorous acid are formed, and when decomposed by carbon dioxide, readily soluble sodium carbonate, that is, all the products of the reaction are completely soluble, and hence no sour is necessary to dissolve them, washing with water being sufficient These reactions are shown in the equations

$$NaOCl+H_2O \rightleftharpoons NaOH+HOCl,$$
$$2NaOCl+CO_2+H_2O \rightleftharpoons Na_2CO_3+2HOCl$$

The bleaching action of a solution of sodium hypochlorite is developed less rapidly, but can be controlled more easily, than that of a solution of bleaching powder This is due to a combination of causes Sodium hydroxide is a stronger base than calcium hydroxide, and its salts are not, therefore, hydrolysed by water to so great an extent. Thus, the free hypochlorous acid in the solution is also less than in a corresponding solution of bleaching powder But sodium hydroxide is much more soluble in water than calcium hydroxide A solution of bleaching powder can never contain more calcium hydroxide than is required to saturate the water When carbon dioxide acts on the solution, some of the calcium hydroxide is removed as calcium carbonate, and this promotes the liberation of more hypochlorous acid by hydrolysis Moreover, when the calcium hydroxide is reduced to a certain point, chlorine is probably produced by a reversion of the equation

$$2CaOH+2Cl_2 \rightleftharpoons CaCl_2+Ca(OCl)_2+2H_2O.$$

Now, in the case of sodium hypochlorite, both the sodium hydroxide and sodium carbonate remain in solution, tending to stabilise it The accumulation retards both the liberation of hypochlorous acid by hydrolysis and also the reversion of the equation

$$2NaOH+Cl_2 \rightleftharpoons NaCl+NaOCl+H_2O$$

It is, in fact, found in practice that the action of atmospheric carbon dioxide in developing the bleaching action of solutions of sodium hypochlorite is comparatively small. It is not unusual to have to neutralise a portion of the

accumulated alkali or render it insoluble by the addition of a soluble salt of magnesium.

This method of replacing a soluble by a less soluble alkali or a strong by a weak alkali is of practical interest. When a solution of a soluble calcium or magnesium salt is added to one containing sodium or potassium hydroxide, the hydroxides of the alkaline earths are formed together with the sodium salt of the acid—

$$2NaOH+CaCl_2=Ca(OH)_2+2Na_2Cl,$$
$$2NaOH+MgSO_4=Mg(OH)_2+Na_2SO_4.$$

Calcium hydroxide is sparingly soluble and magnesium hydroxide almost insoluble in water. If excess of magnesium sulphate be present in a solution of sodium hypochlorite, the sodium hydroxide is removed from the solution as quickly as it is produced by hydrolysis. Magnesium hypochlorite affords an interesting example of the combined effects of hydrolysis and simultaneous removal of the alkali from the sphere of action. It undergoes hydrolysis in accordance with the equation

$$Mg(OCl)_2+2H_2O \rightleftharpoons Mg(OH)_2+2HOCl.$$

Owing to the insolubility of the magnesium hydroxide, there can be practically no alkali in solution, and, hence, nothing to limit the hydrolysis of the hypochlorite As a matter of fact, magnesium hypochlorite is so rapid a bleaching agent that its action is difficult to control.

The Preparation of Sodium Hypochlorite Bleaching Solutions.—Three methods are available—

1. By passing chlorine gas into a cold solution of sodium hydroxide or carbonate

2 By treating bleaching-powder solution with sodium carbonate, sulphate, or hydroxide

3. By the electrolysis of a solution of sodium chloride.

Before liquid chlorine became an article of commerce either methods (2) or (3) were usually employed. Sodium hypochlorite, prepared by the electrolysis of salt, was considerably used at one time It will be described later The production of liquid chlorine in a convenient form and at a reasonable cost now makes it possible to prepare sodium hypochlorite solutions very easily.

When a cold concentrated solution of sodium hydroxide is saturated with chlorine and concentrated at a low temperature, crystals of sodium hypochlorite, $NaOCl\ 6H_2O$, nearly free from sodium chloride, are deposited. Eau de Javelle has been described in Chapter XXIII. Inman (*J. Soc Dyers and Col.*, 1923, p. 81) has proposed preparing this in contact with the cotton It is known that it is difficult to free cotton completely from alkali after the lye boil He suggests that the residual adsorbed alkali could be converted into sodium hypochlorite on the cotton by treatment with chlorine As an alternative it is proposed to soak the goods in a solution of sodium carbonate of suitable strength and then expose them to the action of chlorine gas in a closed chamber, the degree and rate of bleaching being determined by the quantity of chlorine admitted. The process is worth further investigation

Stock or dilute solutions of sodium hypochlorite, containing sodium chloride, can be prepared readily by passing chlorine into a cold aqueous solution of sodium hydroxide or carbonate. But care must be taken to keep the temperature low or sodium chlorate is also formed.

The reactions are—

$$2NaOH+Cl_2 \rightleftharpoons NaCl+NaOCl+H_2O,$$
$$6NaOH+3Cl_2=5NaCl+NaClO_3+3H_2O.$$

Secondly, a little free alkali must be left in the solution. If the whole of the caustic alkali be chlorinated, the solution is somewhat unstable and develops its bleaching action too rapidly. When a neutral bleaching solution is required it can always be made by adding a little acid or magnesium sulphate. A solution containing from 100 to 150 grammes of available chlorine per litre can readily be obtained in this manner The same remarks apply when sodium carbonate is used. The passage of the chlorine through the solution should be stopped directly the evolution of carbon dioxide is observed, indicating that the sodium carbonate has been changed into sodium hypochlorite and bicarbonate—

$$2Na_2CO_3+Cl_2+H_2O=NaOCl+NaCl+2NaHCO_3.$$

The alkalinity of the solution should then be restored by the addition of a little normal sodium carbonate. If the introduction of chlorine be continued beyond this point, hypochlorous acid is liberated and the bleaching liquor is unstable and too rapid in action—

$$2NaHCO_3+Cl_2=HOCl+NaCl+CO_2$$

A solution of sodium hypochlorite can be made, also, by treating a clear solution of bleaching powder with powdered sodium carbonate or sulphate till no further precipitate is produced. The precipitated calcium carbonate or sulphate is then allowed to settle (or the mixture is filtered) and the clear liquor drawn off—

$$(1)\ Ca(ClO)_2+Na_2CO_3=2NaOCl+CaCO_3$$
$$(2)\ CaCl_2+Na_2CO_3 \quad =2NaCl+CaCO_3$$
$$(3)\ Ca(OH)_2+Na_2CO_3=2NaOH+CaCO_3.$$

This process is rather troublesome and a slight excess of sodium carbonate is always present This is not necessarily a disadvantage, since it increases the stability of the solution

A more accurate method is to determine by experiment the correct quantity of sodium carbonate to use, and weigh this out and dissolve it separately in water The bleaching powder is first extracted in the manner already described The clear solution is run into a suitable tank, provided with a sludge cock, by means of which the precipitate may be removed. The liquor is then titrated to ascertain its strength in terms of chlorine or hypochlorite. The alkalinity is also determined, and from these the correct quantity of sodium carbonate is calculated. This is dissolved in water and added to the bleaching-powder solution. After thorough mixing, the precipitated calcium carbonate is allowed to settle and the clear liquor syphoned off for use. If concentrated solutions are required, it is necessary to fortify the first liquor with more bleaching powder and repeat the process, since, after a certain point, the precipitate becomes too bulky to manipulate. Instead of sodium carbonate, sodium hydroxide may be used. The process is exactly the same. The tanks used in all cases must be of stone or cement

A still more accurate method is to determine the total lime present in the bleaching-powder solution. This is done by diluting a measured volume and boiling it with hydrochloric acid till the chlorine is expelled. The solution is then made alkaline with ammonia and any precipitated alumina or iron removed by filtration. The calcium is precipitated by adding solid ammonium oxalate

to the boiling filtrate The precipitated calcium oxalate is filtered off on a Gooch crucible, washed, dissolved in dilute sulphuric acid, and titrated with decinormal potassium-permanganate solution corresponding to 0·002 gramme of calcium, and will require 0·0053 gramme of anhydrous sodium carbonate for its precipitation

Preparation of Sodium Hypochlorite by Electrolysis.—Pure water does not conduct electricity, but when compounds, such as acids, alkalis, or salts, are dissolved in it, the solution becomes a conductor. These substances, which are able to conduct electricity, are termed "electrolytes." Other bodies, such as sugar, do not confer this, however, upon water, and are known as "non-electrolytes" When a current of electricity is passed through a solution of an electrolyte, the latter, as a rule, is decomposed. But the products of decomposition appear only at the electrodes, or plates, immersed in the solution and connected with the poles of the battery

Electrolytes, when dissolved in water, dissociate partially into ions. These may be either atoms or groups of atoms

Thus, sodium chloride dissociates into sodium (Na) and chlorine (Cl) ions, sulphuric acid into hydrogen (2H) and SO_4 ions These ions are charged with equal quantities of positive or negative electricity When they combine to form the molecule of the electrolyte, these charges neutralise each other and the molecule becomes neutral, but when the molecule dissociates, the ions become again charged with equal and opposite charges of electricity This dissociation and recombination is always going on Thus, a solution of sodium chloride in water contains (1) molecules of sodium chloride in which the two charges neutralise each other, (2) sodium (Na) ions charged with positive electricity, (3) chlorine (Cl) ions charged with negative electricity A solution of sodium sulphate, similarly, contains neutral sodium sulphate molecules, positively charged sodium ions, and negatively charged SO_4 ions In general, an electrolyte dissociates into a metallic ion (or hydrogen), and an ion consisting of a group of elements, such as SO_4 The former are charged with positive and the latter with negative electricity. Now, ions charged with positive electricity are attracted to the negative electrode pole of a battery, those charged with negative electricity to the positive electrode Hydrogen and metals which are attracted to the negative electrode are termed "electro-positive," and the other ions "electro-negative" When an electric current is passed through a solution of an electrolyte, by immersing in the liquid two plates or electrodes connected by wires to the poles of a battery, the negatively charged ions are directed towards the positive electrode (called the anode), while the positively charged ions travel towards the negative electrode (or cathode) The ions themselves are termed "anions" and "cations" respectively As these anions and cations arrive at the electrodes their electric charges are neutralised by the opposite electricity of the electrode, and instead of electrically charged ions, the products of decomposition of the electrolyte are apparent. These, in the case of hydrochloric acid, are gaseous hydrogen and chlorine

When a solution of sodium chloride is electrolysed, positively charged sodium ions and negatively charged chlorine ions are directed towards the electrodes. When the sodium ion reaches the cathode and loses its electric charge it becomes an atom of metallic sodium, possessing all the chemical properties of the metal. But sodium decomposes water directly it is brought into contact with it, forming sodium hydroxide and hydrogen—

$$Na+H_2O=NaOH+H.$$

Hence, a solution of sodium hydroxide collects round the cathode, and hydrogen gas is liberated. Owing to these secondary reactions the final products of electrolysis are not necessarily the electrically discharged ions.

This decomposition can readily be illustrated by moistening a piece of filter-paper with a solution of salt and phenolphthalein, and bringing the two terminals of a battery in contact with it. A pink colour is immediately produced at the negative electrode or cathode This test is used also to identify the cathode or anode.

But chlorine and sodium hydroxide react, forming sodium hypochlorite and sodium chloride—

$$2NaOH+Cl_2=NaOCl+NaCl+H_2O.$$

If the two electrodes are separated by a porous diaphragm so that each is in a separate part of the cell, this does not happen, and the products can be collected separately. Chlorine hydrogen and sodium hydroxide are made simultaneously in this way

If the electrodes are not separated, nor any other means provided to prevent it, the sodium hydroxide and chlorine gradually come into contact by diffusing through the water, and sodium hypochlorite is formed Instead of a diaphragm, mercury is sometimes used to keep the sodium and chlorine separate The cathode of the cell is made of this metal It dissolves the sodium as soon as it is liberated, forming sodium amalgam This amalgam, which is constantly circulating, passes at once into another vessel containing water, where it forms sodium hydroxide and hydrogen The mercury then flows back into the cell and receives more sodium.

If the electrodes are, purposely, placed very close together, the sodium hydroxide and chlorine are brought together much more quickly than when the poles are some distance apart, and nearly all of the chlorine is changed into sodium hypochlorite

These are the principles of the electrolyte preparation of this body Both methods may be used, viz —

1. The chlorine and sodium hydroxide may be collected separately and made to react on each other, *i.e* a double cell is used.
2 A single cell is employed, and sodium hypochlorite is produced directly

The second method is more common, the solution of sodium chloride being circulated continuously until a sufficiently high concentration of sodium hypochlorite is produced.

The apparatus used consists essentially of—

1. A tank for the salt solution.
2. An electrolyser and circulating tank.
3. A storage tank for the electrolysed solution

The electrolyser consists of a number of cells The electrolyte passes through these successively between a series of electrodes, between which is maintained a sufficient difference of electric potential to produce a current. The successive arrangement of the electrodes is illustrated in fig 159.

The electrolyte can flow either in series, as in (1), or in parallel stream, as in (2)

The continuous process presents some difficulties These are due, chiefly, to (1) secondary reactions which take place at the electrodes, (2) the simultaneous decomposition of water with liberation of hydrogen and oxygen.

This means that the reactions

(1) $NaCl = Na + Cl$,
(2) $Na + H_2O = NaOH + H$,
(3) $2NaOH + 2Cl = NaOCl + NaCl + H_2O$,

are not the only ones which take place.

The secondary reactions include—

1 Reduction of hypochlorite to chloride by the nascent hydrogen liberated at the cathode—

$$NaOCl + 2H = NaCl + H_2O$$

2 The discharge of oxygen at the anode from the OCl ions, which are formed when a certain amount of sodium hypochlorite has been produced—

$$NaOCl = Na + OCl$$

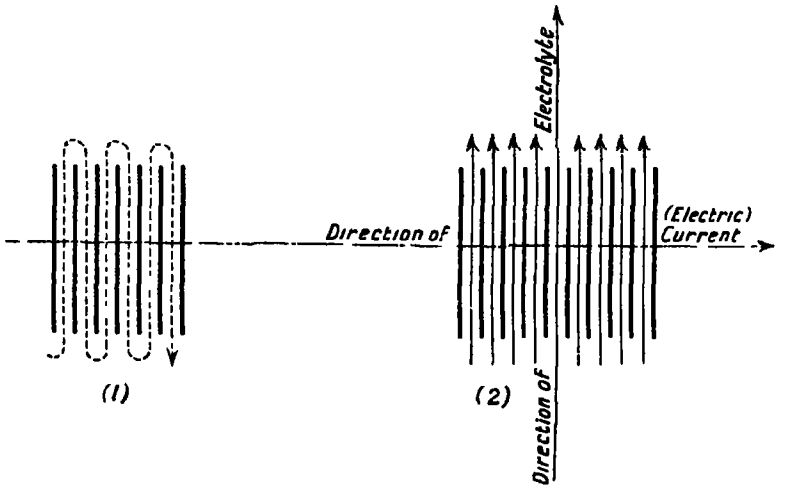


FIG 159.—Directions of current and electrolyte

This action is accompanied by the formation of hypochlorous and chloric acids. Thus

(1) $2OCl + H_2O = 2HOCl + O$
(2) $6OCl + 3H_2O = 2HClO_3 + 4Cl + 4H + 3O$.

3 Oxidation of hypochlorite to chlorate, and also its decomposition into NaCl—

(1) $NaClO + 2HOCl = NaClO_3 + 2HCl$
(2) $NaClO + HCl = NaCl + HOCl$
(3) $2NaClO + O_2 = 2NaCl + 2O_2$.

Chlorates are not easily formed as long as the solution is alkaline. The electrolyte, however, in the neighbourhood of the anode tends to become acid owing to the decomposition of water by the liberated chlorine, in accordance with the equation

$$Cl_2 + H_2O = 2HCl + O.$$

Both the oxygen and hydrochloric acid cause secondary reactions, as illus-

trated above. According to Ahlin (*J S.C.I.*, 1908, p. 409), the formation of chlorates is due not only to the direct oxidation of hypochlorites, but is caused by reaction between the chlorine and OH ions produced from the water—

$$Cl+5OH=HClO_3+2H_2O.$$

The current density also influences these reactions. The accumulation of acid can, of course, be prevented by neutralising the acidity at the anode, but any excess of alkali reduces the bleaching activity of the liquor. Alkali produces stability and militates against rapid bleaching—in fact, when the electrolytic liquor is alkaline, there is little or no saving of available chlorine in comparison with a bleaching-powder solution. The formation of chlorates is also favoured by high temperature. The remedy for this is rapid circulation of the liquor in the cell and cooling externally by means of a water-cooled worm But excessive cooling reduces the conductivity of the electrolyte. The usual temperature employed is about 20° C., with a maximum of 40° C.

The use of horizontal electrodes with the cathode at the top of the cell also diminishes the secondary reactions by allowing the hydrogen to escape rapidly without coming into contact with the hypochlorite, and, by inducing the stratification of the electrolyte, helps to protect the sodium hypochlorite from being attacked by the acids and oxygen.

Not only does oxidation take place at the anode, but corresponding reduction is also set up at the cathode, resulting in the reproduction of sodium chloride The amount of reduction increases with the concentration of the hypochlorite, until ultimately a point of equilibrium is reached, when the hypochlorite is decomposed as quickly as it is formed.

Reduction is, as we have seen, retarded by the horizontal arrangement of the electrodes The escape of the hydrogen in the form of bubbles of molecular, as opposed to nascent, gas is also encouraged by high current density, or the addition to the electrode of such bodies as turkey-red oil, or of small quantities of calcium or magnesium salts. The latter, becoming electrolysed, produce a deposit of calcium or magnesium hydrate on the cathode, in accordance with the equations

$$CaCl_2=Ca+Cl_2,$$
$$Ca+2H_2O=Ca(OH)_2+H_2.$$

This coating does not interfere with the conductivity of the cell, but assists in the liberation of the hydrogen in a molecular state, in which condition it has no action on the hypochlorite It also serves to keep the hydrogen from contact with the hypochlorite at the surface of the cathode. A better effect is produced by potassium chromate, but, owing to its colouring effect, it is not available in the practical production of bleaching liquor. The natural lime and magnesia compounds present in salt are not generally sufficient for the purpose, and must be supplemented by further very slight additions.

Other considerations affecting the secondary reactions are that high current density at the cathode lessens the above-mentioned reduction effect. Low current density at the anode diminishes the liberation of oxygen, and is favourable to the prevention of chlorates, but increases the tendency to discharge of OCl. The most effectual combination of conditions in favour of efficient working are found to be—

1. High current densities at both electrodes.
2. Temperature of liquor about 23° C.
3. Addition of lime or lime compounds to lessen reduction by hydrogen.

4. Horizontal arrangement of electrodes.
5. Fairly rapid circulation of liquor.

Where the vertical arrangement of electrodes is employed, the detrimental mingling of the several constituents of the electrolytic cell is very marked, and it is then more economical to limit the concentration of hypochlorite obtained to a yield of say 9 grammes of chlorine per litre or less

In the other cases the economical yield may be increased to 35 grammes of chlorine per litre, such figures having been obtained by the authors in testing apparatus of the Vogelsang and Kother type respectively.

Sodium Chloride, NaCl.—Since sodium chloride or salt is the raw material for the production of electrolytic bleaching liquors, it may be referred to briefly. It occurs in nature in all parts of the earth, and is the principal constituent of sea-water Rock-salt is found in Cheshire, Worcestershire (Droitwich), Saxony, Austria, Spain, and the United States of America It forms large transparent crystals, which are colourless, grey, reddish yellow, or brown The most important deposits are found in Galicia, where the beds of rock salt are said to be 500 miles long, 20 miles broad, and 1200 feet in depth The Stassfurt salt beds are also important These form the chief source of potassium compounds as well as salt

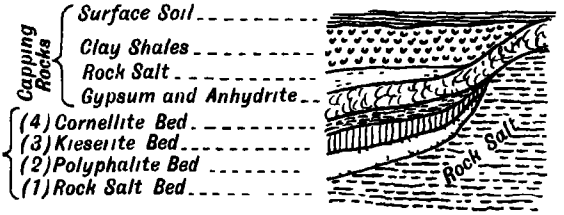


FIG. 160.—Stassfurt salt beds

According to Mellor (*Modern Inorganic Chemistry*, p 224) these beds may be divided into four strata, illustrated in fig 160

1. The rock-salt bed is broken up at fairly regular intervals with 2- to 5 inch bands of anhydrite, $CaSO_4$.

2. The polyhalite bed, which lies immediately above the rock-salt, consists of salt mixed with bands of magnesium chloride and polyhalite, $2CaSO_4\,MgSO_4.K_2SO_4\,2H_2O$

3. The kieserite bed contains rock salt and kieserite, $MgSO_4\,H_2O$.

4. The carnallite bed consists of a reddish layer of rock-salt associated with kainite, $K_2SO_4\,MgSO_4\,MgCl_2\,6H_2O$; carnallite, $MgCl_2\,KCl\,6H_2O$; and other minerals, such as sylvine, KCl, and leonite, $MgSO_4\,K_2SO_4\,4H_2O$.

These deposits are covered with layers of gypsum, $CaSO_4.2H_2O$, anhydrite, $CaSO_4$, rock-salt, bunter clay shales, and finally the surface soil. They are used principally for the preparation of potassium and magnesium salts

Much salt is obtained by evaporation of sea-water, especially in districts where no mineral salt occurs The water is collected in large shallow pools, and allowed to evaporate under the action of the heat of the sun till it begins to crystallise. The crystals are removed by means of rakes as they are deposited. Salt is also obtained from natural salt beds These are sometimes pure enough to dig out, but frequently it is extracted by pumping in water, allowing it to become saturated, and pumping it out again. Most of the impurities are left behind,

and the brine thus obtained is concentrated by evaporation or exposure to air till it crystallises In Hodgkinson's apparatus a series of shallow evaporating pans are used, arranged vertically one above the other The lowest is heated by flue gases The steam given off from the first pan is led through a false bottom to a second, and the process is continued throughout the series Each pan has a mechanical scraper which removes the salt crystals into pockets from which they may be extracted The temperature of the pans is maintained constant, and in this way uniform products are obtained from each pan, the degree of fineness decreasing from the bottom upwards Salt prepared by these methods always contains soluble impurities, such as sulphate of sodium, chlorides and sulphates of calcium and magnesium. Pure sodium chloride is made by passing hydrochloric acid gas into an aqueous solution of common salt till it is saturated, when the salt is precipitated, the impurities remaining in solution. Salt is also recovered as a by-product in the manufacture of glycerin from soap lyes. Sodium chloride forms anhydrous crystalline colourless cubes. When heated it generally decrepitates, owing to the escape of mechanically entangled moisture. It melts at 801° C and boils at 1750° C Salt is moderately soluble in water Its solubility at different temperatures is

0° C	35 63
50° C.	36 67
100° C	39 12

The relation between specific gravity and the concentration of the solution at 15·5° C is given in the following table :—

Specific Gravity	NaCl Per cent	Specific Gravity	NaCl Per cent	Specific Gravity	NaCl Per cent
1 00725	1	1 07335	10	1 14315	19
1 01450	2	1 08097	11	1 15107	20
1 02174	3	1 08859	12	1 15931	21
1 02899	4	1 09622	13	1·16755	22
1 03624	5	1 10384	14	1 17580	23
1 04366	6	1 11146	15	1 18404	24
1 05108	7	1 11938	16	1 19228	25
1 05851	8	1 12730	17	1·20098	26
1 06593	9	1 13523	18	1 20433	26 395

In addition to the impurities mentioned above, traces of iron may also be present The following analyses show the composition of two commercial samples —

	1	2.
Water	0·68	0 70
Sodium sulphate	1 88	1 30
Calcium ,,	0 00	0 85
Sodium chloride	97 44	97 15

The Analysis of Salt.—About 5 grammes of the sample are heated in a weighed flat dish to a temperature of about 110° C. till all the moisture present

is expelled. The residue is then cooled in a desiccator and weighed. If it is yellow or brown in colour iron may be present If the dried residue is ignited very gently, any further loss of weight indicates organic matter

A second 5 grammes of the sample are then extracted with water. The insoluble matter is collected on a weighed Gooch crucible, dried, and weighed. The filtrate is made up to a convenient volume, say 500 c c., with distilled water, and the sodium chloride present is determined by titration with decinormal silver-nitrate solution Calcium sulphates and other impurities are determined in the solution in the manner described for water.

Types of Electrolytic Apparatus.—There are many forms of apparatus designed for the production of electrolytic bleaching liquors A few of these may be described, in order to illustrate the general principles involved. One

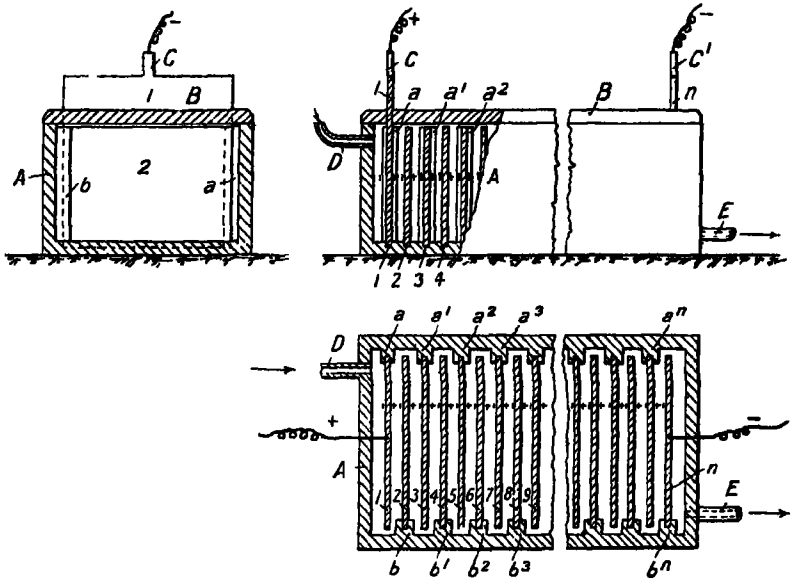


FIG 161 —Kellner electrolyser.

of the first to be used commercially was the Kellner electrolyser (fig 161). Its chief feature was the introduction of bipolar electrodes, in order to avoid multiplicity of contacts and to render the apparatus suitable for using with a current of ordinary standard voltage, such as is employed for lighting. This feature is of interest, because the voltage required for the electrolytic action in any given cell is in the neighbourhood of four volts, and the generation and transmission of electricity at this pressure involves the use of inconvenient or abnormal apparatus. The following description, taken from the patent specification, illustrates the details of the apparatus It should, however, be pointed out that the practice of combining the preparation and use of the liquor as described is to be deprecated, whether in connection with this or any electrolyser, as the impurities introduced into the electrolyte hinder electrolysis.

Kellner's Apparatus (Eng. Pat. 13723) —The apparatus consists of a trough A of non-conducting material covered with a lid B, and provided on two opposite sides with grooved ribs a, a^1, a^2, a^n, and b, b^1, b^2, b^n. These ribs are arranged so

that those on one side face a space between two on the other, and *vice versa*. Electrodes 1, 2, and 3, preferably of carbon, or metal plates covered on one side with platinum, are fitted into the grooves in the ribs, as shown in the figure, so that the free end of each projects into the space between the pair of ribs on the opposite side of the trough. The end electrodes project from the trough through the cover. The liquid to be electrolysed enters A through the pipe D, pursuing a zigzag course between the electrodes, and is discharged through E. The alternate arrangement of the electrodes converts each space between two neighbouring electrodes into a separate cell, one side of each electrode being an anode and the other a cathode. Thus, supposing the current enters at the electrode 1, and leaves at the electrode *n*, the electrode 1 will then be an anode, the side of 2 next the electrode 1 being a cathode, and the further side acting as an anode and so on The arrangement is thus seen to be similar to a series of separate cells arranged in series, only two contacts being necessary, one for the first and another for the last electrode The plan by which the free end of each electrode enters a space between two ribs prevents any portion of the current flowing from the fixed end of one electrode past the free end of the adjacent one, and through the electrolyte to the succeeding electrode. By this means loss of electrical energy is avoided, the current following the path of least resistance, and passing from electrode to electrode direct, without any portion taking the zigzag course followed by the electrolyte. The distance between the electrodes being very small, no diaphragms are used, so that the internal resistance of the apparatus can be made very small As the solution of common salt passes through the cells, chlorine is formed at all the anode sides of the electrodes and caustic soda at the cathode sides. The rapid circulation of the liquid through the cells causes the chlorine formed to be at once brought into contact with the caustic soda, whilst the hydrogen formed at the cathodes is removed rapidly, and prevented from interacting with the sodium hypochlorite formed—

$$2Na+2H_2O=2NaOH+H_2,$$
$$2NaOH+Cl_2=NaOCl+NaCl+H_2O$$

The bleaching liquid is conveyed through E back to the original reservoir, containing the material to be bleached, by means of a pump, so that constant circulation through the bleaching reservoir and decomposing apparatus is maintained. When carbon electrodes are employed, a filter is interposed between the decomposing tank and the bleaching reservoir, this filter may consist of glass-wool confined between perforated metal plates

The Haas-Oettel apparatus recommended by Duckworth (*J S C I*, 1905, p. 1157), from whose paper the following description is taken, consists of an electric cell or electrolyser, made of asphalt composition, placed in a water-tight tank, which is carefully insulated to prevent waste of current The electrodes are on the double pole system, that is, with one pole at each end of the apparatus, and a number of intermediate electrodes that have no contact with each other or with the current, except as the latter passes through the solution. The end and vertical pole electrodes are of carbon, $\frac{3}{4}$ inch thick, reaching to the bottom of the electrolyser. The intermediate electrodes consist of carbon plates, $\frac{3}{8}$ inch in thickness, fitted into grooves on each of the apparatus, and dividing it into numerous cells or compartments. The intermediate electrodes do not reach to the bottom of the tank, and start some distance below the surface They rest upon a non-conducting plate of the same thickness, and support a similar non-conducting plate projecting above the surface of the liquid. This arrangement allows dirt, etc., to collect in the dead or non-conducting space, and since the

liberated chlorine gas has to travel through a considerable head of liquor, it is completely absorbed, and the loss is reduced to a minimum Although the separate cells do not communicate with each other, each has an opening into the tank at the top and bottom The tank is filled with brine till the cells are filled to the top. When the current starts, the liberated hydrogen gas causes the liquor to overflow into the tank through the upper opening, and thus continuous circulation is maintained, more liquor being drawn in to replace the overflow through the lower opening. The current used is a continuous one of 110 volts. The temperature is regulated by means of water coils and not allowed to rise above 28° C

According to Reuss (*Electrical Review*, 1911, p 410) the yield of a modern Oettel electrolyser with carbon electrodes is at the rate of about 8·4 kw hours and 10·7 kg. of salt per kilogramme of available chlorine For an electrolyser producing 10·5 kg of available chlorine, the cost of replacing electrodes is about £4, 10s. per annum

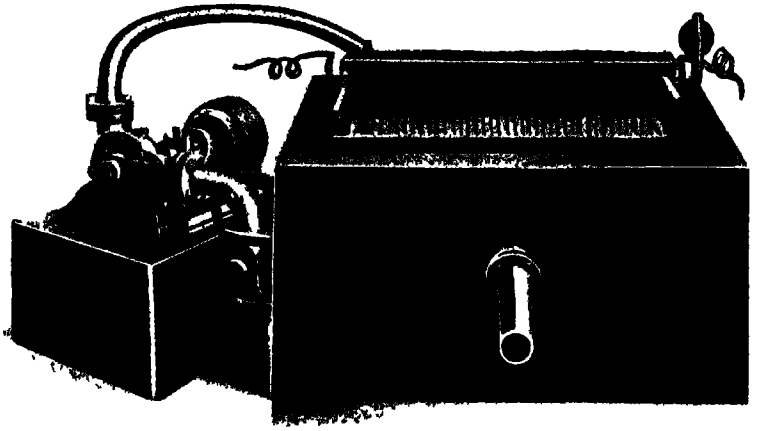


Fig 162.—Vogelsang electrolyser

Kellner (*J S C I*, 1901, p. 131) uses more dilute solution of sodium chloride than Haas and Oettel He maintains that, although at a lower concentration more electrical energy per kilogramme of active chlorine produced is required, the extra cost of energy is balanced by the lower consumption of salt. Tests carried out by him with apparatus of the Kellner and Haas and Oettel types under similar conditions seem to prove that the Kellner form is cheaper, owing to the greater current density employed.

Vogelsang's apparatus (fig 162) embodies the same principle as the Kellner, but is built with considerably less expenditure of platinum to effect the same output. The electrodes extend the full width of the containing vessel, and the flow of liquor is under and over the bipolar electrodes (fig 163). The economy of platinum is effected by building the electrodes of slate bars, around which are folded in zigzag form a sheet of platinum-iridium foil 0·03 mm thick, and presenting active faces on opposite sides of the electrodes. The product of the width of the electrode across which the foil extends, and the thickness of the foil, presents a conducting area adequate to the passage of the current between

the active faces. The result is a cheap electrode of great mechanical strength and capable of effecting high current densities inadmissible with carbon electrodes.

The use of the exceedingly thin platinum foil in these electrodes would be inadmissible unless protected, as described, by insulating plates placed behind the anode and cathode surfaces. The reason for this is not merely on account of the mechanical support which they afford, but because it is found that if the electric current be allowed to pass straight through the foil, perforation of the foil is produced. If, however, the anode and cathode surfaces of the same foil be not placed immediately opposite one another, and are also backed with insulators, this perforation does not take place.

An important consideration in the arrangement of electrodes is the pro-

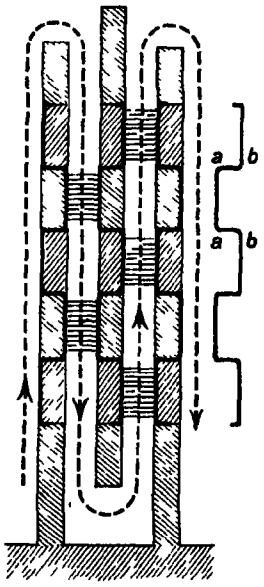


FIG. 163.—Vogelsang electrodes.

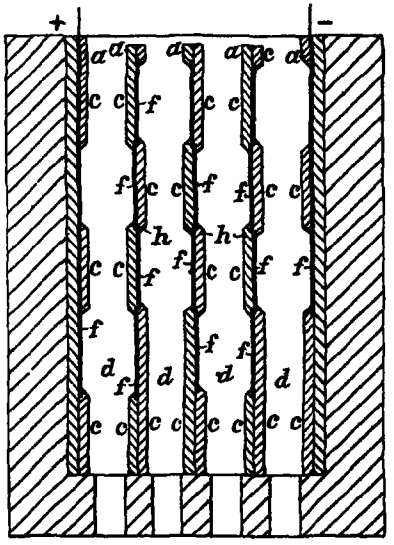


FIG. 164.—Thorp electrolyser.

portioning of the sectional area conducting the current through the electrode, and also the superficial area in contact with the electrolyte. The former affects the losses of power in transmission through the electrodes, and the latter has been already referred to as bearing on the secondary losses occurring during electrolysis In the Vogelsang electrodes the allowance for the current density in the former respect is at the rate of 25 amp per square centimetre, and in the latter, 50 amp. per square decimetre.

It is found that calcareous deposits from the electrolyte are apt to form on the insulating plates, and occasionally require removal by washing or a mechanical scraping.

In the Thorp electrolyser (fig. 164) a sheet of platinum foil is supported by insulating plates fixed on its opposite sides, and slightly overlapping each other where they join. The amount of inactive foil, which serves merely to conduct the current from a cathode and anode of the same foil, is thus reduced, with corresponding saving in platinum, also the anodes are protected from mechanical

injury during the occasional removal of the accumulated deposits from the insulators.

A cheaper form of electrode is made by Kother (fig 165), in which the anode is made of platinum foil and the cathode of graphite, as it is found that it is possible to use a carbon electrode for the cathode with tolerably good results and considerable reduction of initial cost.

The disintegration of the platinum foil in the manner above mentioned is prevented in the Kother electrode by inserting an insulating substance, such as glass, between the interior surfaces of the two elements Electrical continuity is effected by connecting the elements at their edges where they are out of contact with the electrolyte. This electrode may be used either vertically or horizontally

Despite the various methods adopted to increase the utility and efficiency of vertical electrodes, the maximum economy and production of concentrated solutions of hypochlorite in an open cell can only be obtained by arranging the electrodes horizontally, for the reason already given

The accompanying drawing illustrates an apparatus designed by Thorp (fig 166), on the basis of Kother's patent, in which the platinum electrodes are arranged horizontally. By the arrangement of the cells in a series of steps the

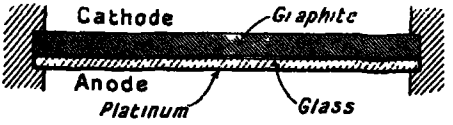


FIG 165.—Kother's composite electrode

bipolar electrodes, which consist of narrow strips of foil serving adjacent cells, assume a simple and economical form

The flow of liquor through the apparatus is effected endwise, either in series or in parallel streams. This apparatus produces a concentration of hypochlorite, indicating a strength of 35 grammes of chlorine per litre when small quantities of lime and turkey-red oil are used with the electrolyte, and the expenditure of salt and power represent a working cost not exceeding £4, 10s. for the equivalent of one ton of bleaching powder under the conditions normally obtaining in bleach-works

Finlay's cell is characterised by the use of a double diaphragm (*Science Abstracts*, 1910, p 14) and central brine compartment, the brine flowing continuously from the central compartment through the diaphragm to the anode and cathode compartments, and thence to suitable outlets. The compartments are made by placing thin rectangular frames of waxed cardboard, about 2 to 3 mm thick, between the diaphragms, which consist of asbestos The layers of the electrolyte are thus simply thin sheets of liquid in which the electrical resistance per square foot is reduced to a minimum The anodes are made of rods of Acheson graphite and the cathodes of sheet iron. The counterflow of the electrolyte aids in reducing the loss of efficiency caused by the passage of hydroxyl ions to the anode, and by diffusion and convection of the dissolved chlorine to the cathode A feature of the cell is the absence of secondary reactions.

In order to obtain bleaching solutions the chlorine and sodium hydrate may be mixed outside the cell.

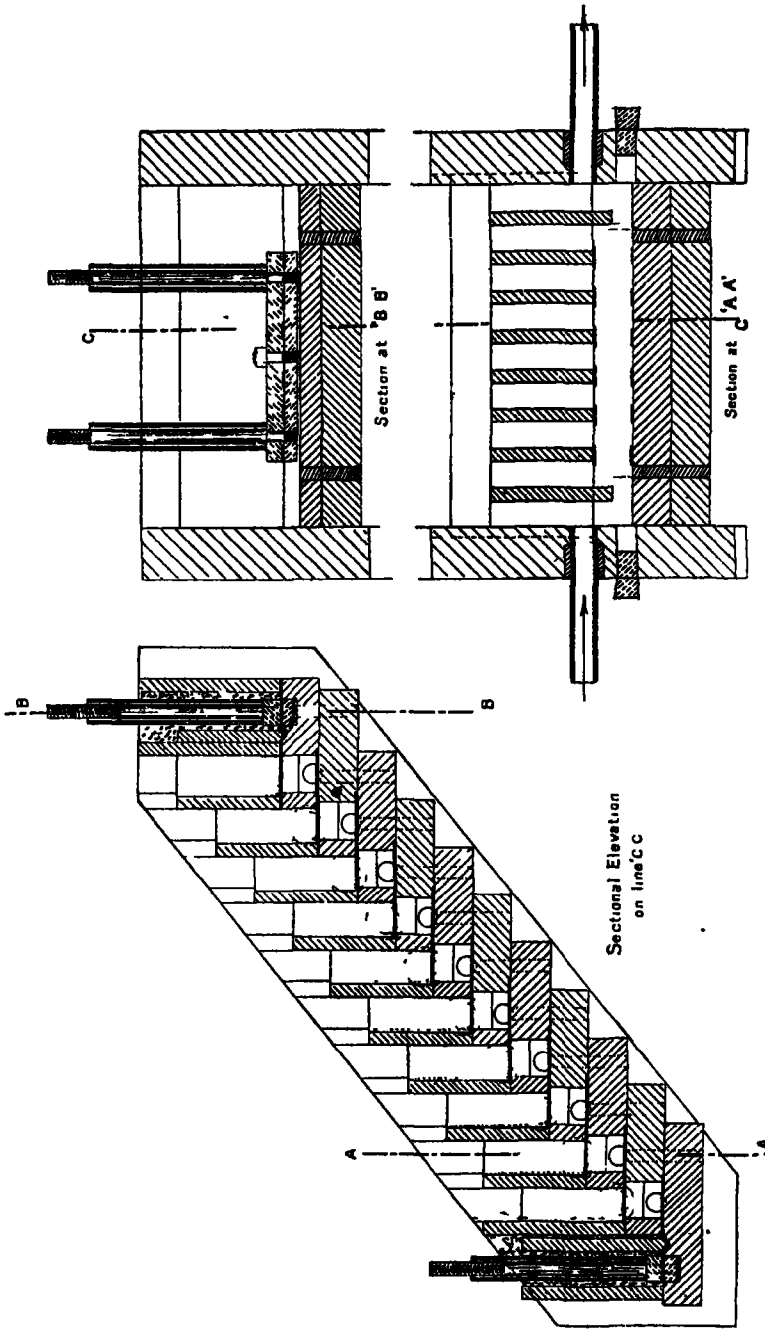


FIG. 166.—Kother's type of electrolyser.

G. Grant Hepburn (*J Soc Dyers and Col*, 1924, p 251), in a comprehensive paper, brings the subject up to date, and from which the following description is taken. The conditions which an electrolyser should fulfil are—

1 Long life of the constructional materials
2 The constructional materials entering into the design must be such that they are not the limiting factor in output
3 Minimum current leakage
4 The greatest possible simplicity of feed to, and delivery from, the individual cells, condition (3) being specially borne in mind
5 Working costs per kilogramme of chlorine to be not greater than those of any other apparatus producing electrolytic sodium hypochlorite

The electrolysers made by Messrs Mather & Platt, Ltd, fulfil these conditions. The following information concerning these is given by the makers —

The Seventeen-cell Horizontal Flow Type —The electrolyser shown in fig 167, designed for medium outputs, consists of a shallow rectangular container of special

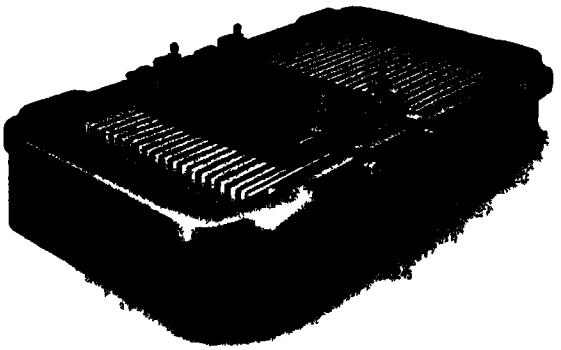


Fig 167 —Patent electrolyser—horizontal flow type

glazed earthenware, divided into a number of cells by plates of graphitic carbon The channels between the carbon plates are continued at either end by walls formed of glass plates, of such cross section as to restrict the flow to the appropriate rate, and to prevent leakage of current through the electrolyte A chamber in one end of the container receives the electrolyte from the pump, whence it flows over a glass weir into the several channels This ensures an equal flow through each cell At the other end of the cell the channels deliver into a second chamber from which the electrolyte falls into the circulating tank below Two end carbon plates form the terminal electrodes, and are connected to the positive and negative poles of the dynamo or source of electric supply It will thus be observed that there is nothing used in the construction of the cell which is, or can be, acted upon chemically by the solution, or electrolytically by the electric current, except the carbons These can be very easily removed and replaced at small cost

The electrolyser—or electrolysers, if several are necessary for the required output—is installed above a tank containing the brine solution, prepared by dissolving common salt, as free from impurities as can conveniently be obtained, in pure water The pump draws the brine from this tank and delivers to the container, whence it again falls into the tank When the brine flows from the

exit end of the electrolyser, the current is switched on. A lively evolution of hydrogen at once takes place in the cells and a slight smell of chlorine is noticeable, but it is of no consequence. The direction of flow of the current should be reversed at the stated intervals mentioned in the working instructions, by means of the change-over switch

When by the passage of the current the brine has been brought up to the required degree of chlorine strength, it is pumped into the storage tank, which should be covered over, as the liquid slowly deteriorates when exposed to air and light. The deterioration is very gradual, and the bleaching liquor may be stored, if necessary, for two or three days; it is better to use it the same day as, or the day after, it is made. The bleaching solution prepared as described may be stored at 1·2 per cent. chlorine strength, and reduced by addition of water to any desired strength, according to the requirements of the particular bleaching operation

In general, it is found that a 15 per cent. salt solution is the most economical to use; brine of this strength is made by dissolving 1½ lbs. of salt in 1 gallon of water The solution is circulated by a pump through the electrolyser at approximately 7 gallons, or 30 litres per minute per electrolyser. The circulation of the brine and the passage of the current are continued till the brine contains from 12 to 12½ grammes of available chlorine per litre During this period the temperature of the brine as observed at the inlet end of the electrolyser must be kept within the limits, of 22° to 32° C, and must not be allowed to rise above 32° C at this point The cooling pipes in the tank into which the electrolyser delivers provide the means of controlling the temperature

The standard electrolyser of seventeen cells is designed for 100 to 110 volts. Two electrolysers should therefore be placed in series, if the pressure available is 200 to 220 volts The current required for the full output of the standard "cell" is 80 to 100 amp When working with the strength of brine and with the currents above mentioned, a standard electrolyser will produce 2½ to 2¾ lbs. of chlorine in one hour, if the electrolyte be worked up to 1·2 per cent. of chlorine strength, or 12 grammes of chlorine per litre of electrolyte To state the output otherwise: To produce 1 lb of active chlorine, 4 to 4⅓ kw hours of electricity and 12·5 lbs. of salt are required.

For larger outputs any number of standard electrolysers may be placed *in parallel* electrically and worked from the same mains, or groups of two or three electrolysers coupled in series may be placed in parallel with each other.

The press or vertical type (fig. 168) is designed for large outputs This electrolyser has twenty-three electrodes giving twenty-two cells, which are mounted transversely on longitudinal steel bars covered with soft vulcanised rubber tubing. These, together with the rubber gaskets forming the side and bottom walls of the cells, are screwed up tightly after the manner of the plates of a filter-press. The electrolyte contained in a concrete tank (circulating tank) is pumped at about 80 litres a minute into an overhead cast-iron vulcanite-coated distributing trough, from which it overflows by a weir on to the perforated distributing tray of pure, hard vulcanised rubber The trough is pivoted at one end on the framework of the electrolyser, and has a screw adjustment at the other, so that the weir is readily set dead-level. From the perforated tray, the electrolyte runs into the troughs carved out of the upper part of the electrodes, passes downwards, through the cells, issuing by the cell ports into the exit channels, and escapes through the syphon outlets. From these it drops back into the circulating tank, or, when there are several electrolysers in the same installation, into a cement channel which delivers into that tank The current

is led to and from the electrolyser by lead cast into the substance of the two end electrodes coupled up to the leads of the dynamo. The details of output are—

A 12·5 per cent. solution of salt is the most economical to employ. It is circulated at a rate of approximately 18 gallons or 80 litres per minute. The circulation of the brine and passage of the current are continued till the brine contains from 11 to 12 grammes of available chlorine per litre. During this period the temperature must not rise above 32° C. The standard electrolyser with twenty-two cells is designed for 100 to 110 volts, and the current required for the full output is 225 to 250 amp. When working with the 12·5 brine solution the standard electrolyser will produce about 9 lbs. of available chlorine per hour if the electrode be worked up to a strength of from 10 to 11 grammes of available chlorine per litre.



Fig. 168.—Patent electrolyser—vertical flow type.

Hepburn gives the following details :—

Current.—100 to 110 volts, 250 amp

Output.—About 4 4 kg. of available chlorine per hour.

Cost per Kilogramme of Chlorine.—(*a*) For salt, 10½ kg., (*b*) for power, 6 to 6·5 kw. hours

Chlorine Strength.—11 to 12 grammes per litre of electrolytic.

With power at ½d. per unit and salt at £1 per ton, the cost of electrolytic chlorine is 2·6d. per pound, with power at ¾d. per unit and salt at £1 per ton, 3·3d. One pound of chlorine from bleaching powder at £10 a ton costs 3d.

In the press electrolyser a container with its attendant disadvantages is dispensed with, the cells being kept full of the electrolyte, and the continuous flow provided for, by maintaining a continuous feed to, and a hydrostatic head in, the upper part of the individual cells, with no liquid communication between adjacent cells in that part, and a separate and insulated outlet for each cell. The head is formed by using graphite electrodes of such a thickness that a suitable trough or reservoir can be formed in their top parts and feeding this by a distributing tray placed about 1 foot to 18 inches above it, in the bottom of which there are perforations. In falling from the trough the numerous streams of electrolyte break up into drops, and current leakage is thereby made

impossible by way of the feed to the cells. The way in which the reservoirs are formed in the graphite is shown in figs 169 and 170

The perforated distributing tray is common to all the cells of the electrolyser. Its width is considerably less than the length of the ridge (2) in fig. 169, so that

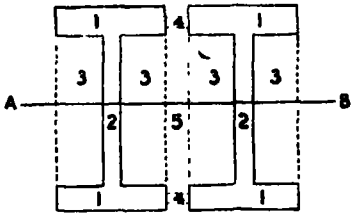


FIG 169.—Top of two electrodes in plan

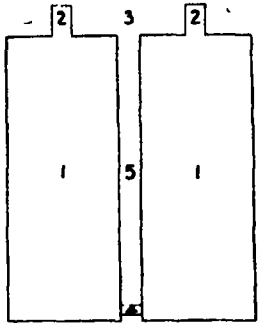


FIG 170.—Vertical section of two electrodes through AB (fig. 169)

(1) Graphite, (2) graphite ridge forming a wall of the excavated trough (3), (4) soft vulcanised rubber forming the side and bottom walls of the cell (5)

a slight splash caused by the falling drops falls within the parts marked (1) and (1) By carrying the rubber side walls ((4) in fig 170) of the cells not quite up to the upper surface of the electrodes, an overflow for the trough is provided, thus obviating the flooding of the troughs and short circuiting of adjacent or of all the cells. By the lateral projection of the electrodes beyond the rubber

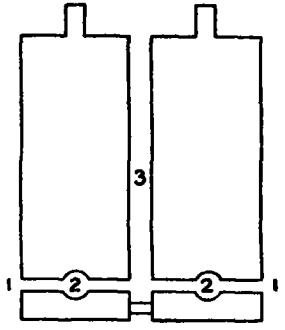


FIG 171.—Vertical transverse section through two electrodes.

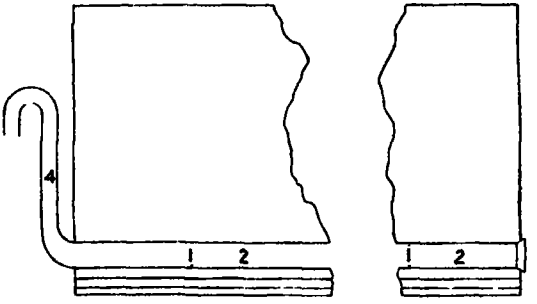


FIG. 172.—Vertical longitudinal section through an electrode.

wall the overflow is confined within narrow limits (thus again preventing leakage), and is subject to electrolysis in its downward course. The exit for the electrolyte is made by boring transverse ports in the lower part of the electrodes, communicating on the one hand with the cells on both sides of the electrode, and with a central channel bored at right angles to the ports (fig. 171). Each central channel is closed at one end and, at the other, is fitted with a perforated rubber stopper carrying a glass syphon. The effluent from this, charged with

bubbles of hydrogen, is given such a distance of free fall that current leakage is again absolutely avoided (fig 172).

The Graphode electrolysers are made in four different sizes, taking respec-

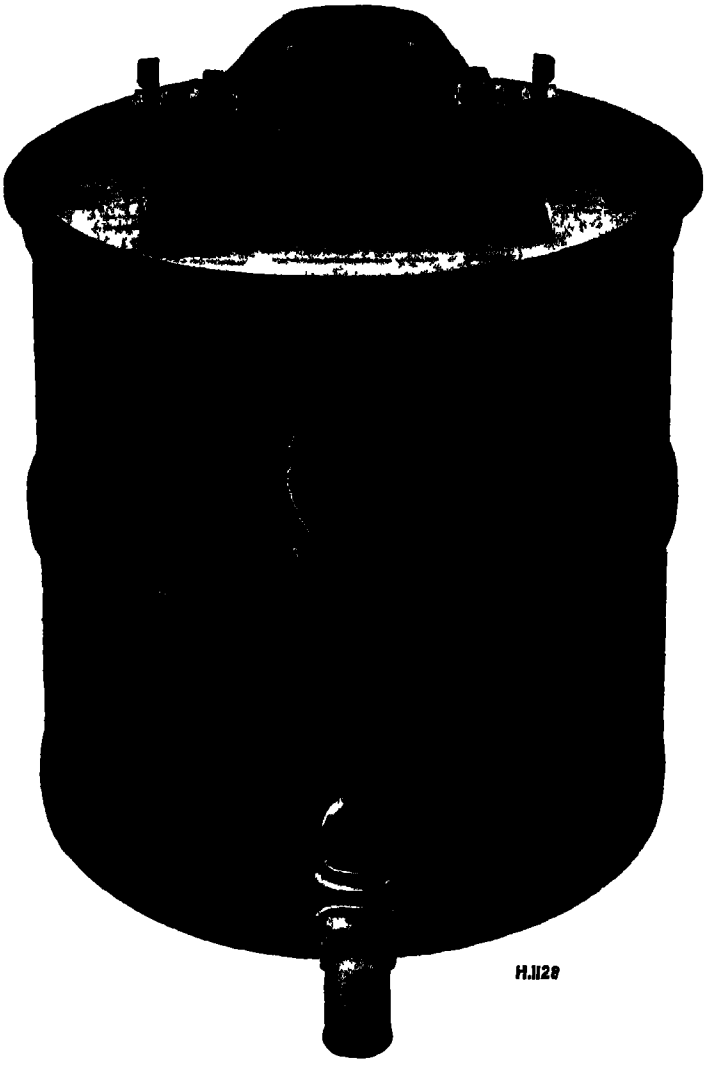


FIG. 172A.—Thirty-ampere Graphode electrolyser.

tively 5, 12½, 30, and 60 amp. The 30-amp electrolyser is illustrated in fig. 172A (H. 1128) It consists of a vulcanite holder, with graphite electrodes, forming eight compact cells The whole stands in a vulcanite container and is almost immersed in the electrolyte Cooling pipes of lead are provided in the containing tank. When a salt solution of from 12½ to 15 per cent. strength is used, an output of 3½ gallons per hour of sodium hypochlorite is obtained, con-

taining 1 per cent. of available chlorine The 60-amp electrolyser is similar to the 30-amp size, but contains nine cells It gives 36 gallons per hour of sodium hypochlorite, containing 1 per cent of available chlorine

The Relative Efficiencies of Bleaching Powder and Electrolytic Solutions. —Considerable difference of opinion exists as to whether bleaching powder or electrolytically produced hypochlorites are the more efficient and economical Different workers have obtained very varying results, due probably to the difficulty of making strictly comparable experiments There can be no doubt, however, that electrolytic solutions are more convenient to handle, are cleaner, and that goods so treated are more readily washed, owing to the greater solubility of sodium salts over those of calcium Undoubtedly, also, in some cases where electricity can be cheaply produced, they are more economical, and where strong solutions are required less danger of tendering results The supporters of the electrolytic bleaching processes, however, often assume that there is some inherent difference in the chlorine evolved which gives it a greater chemical activity This, however, cannot be maintained The following are the chief advantages claimed for the use of electrolytic chlorine —

1 Greater convenience in handling

2 Greater cleanliness

3 Production of more uniform results owing to the greater solubility and diffusibility of sodium salts and greater durability of whiteness

4 Absence of harshness and tendering, which sometimes results when bleaching powder is used

5 Economy in time and materials

6 Economy of chlorine, *i e* with the same amount of chlorine present an electrolytic liquor produces a better result One hundred parts of chlorine from bleaching powder are said to be required to do the same work as from 81 to 95 parts produced electrolytically

7 Greater cheapness of production

Convenience in Handling and Cleanliness —The production of the bleaching solution when and as required is of considerable advantage, since it saves the storing of an unstable body like bleaching powder, and salt can be kept indefinitely without deterioration For small users this is an important point, especially as electrolytic cells may be made of any required capacity The trouble of extracting bleaching powder completely is also avoided, since the bleaching compound is in solution from the start The loss of bleaching powder on extraction frequently amounts to nearly 10 per cent The bleaching solutions are also undoubtedly cleaner, and require very little filtration or sedimentation, owing to the comparative ease of obtaining practically pure salt

Greater Uniformity of Results —Many observers maintain that better and more durable whites are obtained with electrolytic liquors than with bleaching powder Some doubt, however, exists upon this point, but it is certain that the greater solubility and diffusibility of sodium salts over those of calcium must tend to produce better penetration of the goods, hence there is less likelihood of under- or over-bleaching This result may also be assisted by the fact that the electrolytic solution is alkaline, and that the bleaching action is more regularly developed than in the case of bleaching powder

Harshness and Tendering —Chiefly owing to the action of carbon dioxide, calcium carbonate is always deposited in the fibre during bleaching with calcium hypochlorite It is very difficult to bleach with bleaching powder and remove every trace of lime from the goods by washing. This is largely owing to the

limited solubility of calcium sulphate. A very small quantity of lime gives a harsh feel to cotton, and interferes seriously with the production of level colours in subsequent dyeing Owing to the practical absence of lime in the electrolytic solution this difficulty does not arise. Of course it is quite possible to free goods from lime by careful washing, but in practice it is very often imperfectly done. In many cases it does not matter, but for fine goods the electrolytic process is undoubtedly superior from this point of view On the other hand, for certain classes of Lancashire goods harshness is actually desired, and one of the objections urged against the use of sodium hypochlorite is that it does not assist the finisher in this direction. Tendering is also less frequently found in goods bleached with hypochlorite.

Economy of Materials and Plant—Far less acid is required after chemicking with sodium hypochlorite, since there are no insoluble compounds to remove. In fact, it may in many cases be dispensed with altogether In some special cases the plant required is also simpler, the whole of the operations can be carried out in the same vessel, owing to the ready solubility of the bodies used. With a satisfactory plant there is also no waste of chlorine

Economy of Chlorine—It is upon this point that great differences of opinion exist Many observers state that the chlorine obtained by electrolysis is inherently more active than the equivalent from bleaching powder This necessitates the assumption previously referred to, that it is in a different chemical condition, or that the combination between chlorine and soda in sodium hypochlorite is different from that between chlorine and lime in bleaching powder, or that we are dealing with two allotropic forms of the element, one of which is, in fact, more active Thus Fraas concludes as the result of many experiments that—

1. Using equal amounts of available chlorine and working under similar conditions, the electrolytic bleaching liquor gives the better bleaching effect

2. If the bleaching effect be stopped at the same degree of whiteness, the use of electrolytic liquor makes a saving of 5 per cent of chlorine when working with alkaline solutions

3 The presence of excess of bleaching liquor does not alter these comparative results

4. Increase of alkalinity diminishes the rate of bleaching, but increases the final effectiveness of the bleach, both in the case of the electrolytic and bleaching-powder solutions.

Others, however, contend that there is no difference between the chlorine in the two cases, and that solutions containing equivalent quantities of available chlorine have in both cases the same bleaching value, the difference in observed results being due to the difficulty of making strictly comparable experiments, and being within the allowable limits of error, having regard to the nature of these experiments

Duckworth (*J.S.C.I.*, 1905, p. 1157) states, as the result of long experience, that 3 lbs of electrolytic chlorine will do the work of 4 lbs. produced from bleaching powder, and will do it better, quicker, and more easily. Thus 45 lbs. of active electrolytic chlorine are equivalent to 60 lbs. of available chlorine from bleaching powder Some even claim that the proportion of 1 to 2 is nearer the truth. Against this, others urge that it is only a question of time, *i.e.* the chlorine from bleaching powder will do the same work, but requires a longer time to do it. Thus magnesium hypochlorite acts even more quickly than sodium hypochlorite, but is not really more efficient.

W. H. Walker (*J.S.C.I*, 1905, p. 1160) considers that there is a difference between available chlorine and bleaching power, and that although two solutions may have the same oxidising power, as equivalent solutions of bleaching powder and electrolytic chlorine have, it does not follow that they will also have the same "bleaching ability."

Cost of Production.—Even greater difference of opinion is found upon this point than upon the relative efficiency of the two processes. On the one hand, it is maintained that electrolytic chlorine is actually the cheaper to produce, and, on the other, it is said that it is no cheaper, or, if anything, often dearer, but that the results obtained outweigh the increased expenditure. The cost of production depends very much upon the price of salt and electricity Where both are cheap, or where water-power is available, the cost is small. The initial cost depends largely upon the nature of the electrodes. Platinum is very expensive to begin with, but costs little in upkeep. Carbon electrodes are cheap, but require frequent renewal. The following are some recorded cases of comparative cost. In one case recorded in the *Manchester Guardian* (15th October 1909) a 15 per cent solution of common salt was electrolysed to give a solution of chlorine containing 30 grammes per litre at a cost of 7½d. per kilogramme when the most expensive method of producing the current was used, while, when water-power was employed, it was only ½d. per kilogramme

Carey, while admitting that in certain cases electrolytic chlorine may be produced more cheaply than from bleaching powder, contends that as a general rule it cannot be He gives the following figures as a basis for comparison [1] The price per kilogramme of chlorine from bleaching powder at £4, 10s. per ton is 3·1d The power required per ton of chlorine in the various electrolytic cells varies apparently between 6900 and 9000 k w h per ton The salt required per ton of chlorine in the case just referred to was 7 of salt to 1 of chlorine Taking the salt at 12s. per ton, it is equal to a charge of 1d per kilogramme of chlorine. The following table then gives the cost for power and salt per kilogramme of chlorine, with different prices for power, but exclusive of those important items which can be inserted for each special case separately, viz. labour, repairs, interest, and depreciation.

Price k w h	Cost of Power per Kilo Chlorine.	Cost of Salt per Kilo Chlorine.	Cost of Power and Salt per Kilo. Chlorine.
¼d.	1·7d to 2 2d.	1d.	2·7d to 3·2d.
½d.	3 4d. ,, 4 4d	1d.	4·4d. ,, 5·4d.
1d.	6·8d. ,, 9d.	1d.	7·8d. ,, 10d.

This table does not include figures for the production of chlorine by power generated with one of the cheap water-powers, as bleaching works adjacent to such water-power stations are too few to be of any general interest. He contends, therefore, that, with power at ¼d. per k w h when labour, repairs, and capital charges are included, electrolytic chlorine is certainly more expensive than chlorine derived from bleaching powder.

Regarding the matter from the standpoint of the relative bleaching efficiencies of the electrolytic liquor and that derived from bleaching powder, and also allowing for the wastage of chlorine from bleaching powder which

[1] All costs are based upon pre-war prices

arises through storage and extraction, the foregoing figures are subject to some modification Allowing for a wastage of 10 per cent, the cost per kilogramme of available chlorine from bleaching powder at £4, 10s per ton and containing 35 per cent of chlorine will be 3·4d. Taking the respective activities of the two liquors in the ratio of 5 to 4, and 7 k.w.h. and 10 kg. as the average expenditure on power and salt, the following figures result A fair allowance for capital charge is ½d per kilogramme of chlorine produced, and is included. Examples (*a*) are for cases in which the cost of electrical power is known. Examples (*b*) indicate the cost when the charge for power is confined to that of the fuel consumed in running, say, the lighting dynamo during the daytime for electrolysing. The consumption is taken as 3 lbs of coal per b h p, and the efficiency of conversion as being 85 per cent The figures in the last column represent the cost in pence of the equivalent of 1 kg of chlorine in bleaching powder liquor.

(*a*) Power at ½d.	per k w h	, salt at 12s	per ton;	cost is				4 3d
,, ¾d	,,	,,	,,	,,	,,			3 4d.
,, ¼d	,,	,,	,,	,,	,,			2 8d.
(*b*) Coal at 12s	per ton	,,	,,	,,	,,		.	3 1d
,, 10s.	,,	,,	,,	,,	,,	.		2 9d
,, 12s	,,	,,	16s	,,	,,	.		3 4d
,, 10s	,,	,,	,,	,,	,,		.	3 1d

According to Haas and Oettel (*J.S C.I.*, 1901, p. 131) the cost of production of the active chlorine increases with the concentration. Thus the same quantity of chlorine can be produced more cheaply at a strength of 3 grammes of chlorine per litre than at 6 or 10 grammes per litre This only applies to certain apparatus

Jaeglé (*J S.C.I.*, 1905, p 94) found from a series of trials, extending over nine months, that the cost of the bleaching liquor, measured in terms of available chlorine, was practically the same, viz 0·04 mark per kilogramme, whether made from bleaching powder or by electrolysis

Higgins, as the result of numerous experiments, supported also by Ermen, came to the conclusion that from no point of view was an electrolytic bleach better than an equivalent solution of bleaching powder or sodium hypochlorite, while with salt at 23s a ton and electricity at 0·75d per unit it is twice as expensive

From the above illustrations it is obvious that the question of cost is mainly dependent on local conditions affecting the price of bleaching powder, power, and salt. The remaining condition affecting the question is the correct value to assign to the respective bleaching efficiencies of the two forms of the bleaching liquor, and the wastage already referred to, and it has been shown that there is no difficulty in determining the cost for a given set of conditions Moreover, the method of operation can be so adjusted between expenditure of power or salt as to meet the case in which the one or the other may, for local reasons, be the more costly.

As regards concentration of chlorine, electrolysers are now made to produce the liquor at any desired concentration up to 35 grammes of chlorine per litre, and the higher concentrations are for the most part the more economical to produce.

Other Bleaching Agents.

All the oxides of chlorine have oxidising and bleaching properties, although only the derivatives of chlorine monoxide, the hypochlorites, have much practical importance.

Chlorous Acid, $HClO_2$.—This acid is obtained together with chloric acid, $HClO_3$, when chlorine peroxide is dissolved in water—

$$2ClO_2+H_2O=HClO_2+HClO_3.$$

The reaction is analogous to that which takes place between nitrogen peroxide and water—

$$2NO_2+H_2O=HNO_2+HNO_3.$$

Chlorine peroxide is an explosive gas which condenses to a liquid at 90° C. It has a reddish-yellow colour and a characteristic chlorine-like smell. It is obtained when a mixture of potassium chlorate and sulphuric acid is warmed gently. The sulphuric acid first liberates chloric acid, $HClO_3$, which is then decomposed, forming perchloric acid, $HClO_4$, chlorine peroxide, and water—

$$KClO_3+H_2SO_4=KHSO_4+HClO_3,$$
$$3HClO_3=HClO_4+2ClO_2+H_2O.$$

When a saturated solution of chlorine peroxide in water is cooled to a low temperature, crystals are formed which are said to have the composition $ClO_2.8H_2O$ When an aqueous solution of chlorine peroxide is allowed to stand it is changed gradually into a mixture of chloric and hydrochloric acid. Chlorous acid is not known except in solution, but some of its salts are more stable. If an aqueous solution of potassium hydroxide is treated with chlorine peroxide a mixture of chlorite and chlorate of potassium is formed—

$$2KOH+2ClO_2=KClO_2+KClO_3+H_2O.$$

Chlorites, like chlorine peroxide, are very unstable compounds, decomposing with explosive violence when heated. Both chlorites and chlorous acid in aqueous solution are powerful bleaching and oxidising agents

Chloric Acid, $HClO_3$.—This acid is regarded as the hydrate of the hypothetical pentoxide, Cl_2O_5, which combines with water in a similar manner to nitrogen pentoxide—

$$Cl_2O_5+H_2O=2HClO_3,$$
$$N_2O_5+H_2O=2HNO_3.$$

Chloric acid may be prepared from barium chlorate by treating it with cold dilute sulphuric acid—

$$Ba(ClO_3)_2+H_2SO_4=BaSO_4+2HClO_3.$$

The insoluble barium sulphate is filtered off and the filtrate is concentrated *in vacuo* over sulphuric acid Chloric acid is a colourless, unstable liquid, which decomposes readily into perchloric acid, chlorine peroxide, and water, either when heated or exposed to light. It is a very powerful oxidising and bleaching agent. When present in bleaching liquors it always produces oxycellulose and tendering. Chloric acid is monobasic, giving salts termed chlorates. Some of these, such as sodium chlorate and barium chlorate, are important. The former is used as an oxidising agent in dyeing with aniline black. The chlorates are all soluble in water. Their solutions do not give a precipitate with silver nitrate. When chlorates are heated they give up oxygen and are converted into chlorides—

$$2NaClO_3=2NaCl+3O_2.$$

Barium chlorate may be used (Thomson, *J. Soc. Dyers and Col.*, 1916, p. 166) for removing cotton ground-work in lace embroidery. The backing fabric is

treated with a solution of the salt When dried and heated for some time at a temperature of 320° F. it becomes disintegrated and can be brushed out, leaving the embroidered part intact.

The chlorates of potassium, sodium, calcium, and barium may be made by passing chlorine gas into a boiling solution of the metallic hydroxide. This has been referred to previously. They are obtained also when a hot solution of a chloride is electrolysed. The possibility of their production during the preparation of electrolytic bleach liquors has been mentioned

Perchloric Acid, $HClO_4$.—This acid is produced when chloric acid is heated or exposed to light, or when potassium perchlorate is heated with sulphuric acid—

$$3HClO_3 = Cl_2 + HClO_4 + 2O_2 + H_2O,$$
$$2KClO_4 + H_2SO_4 = K_2SO_4 + 2HClO_4.$$

Potassium perchlorate is formed when potassium chlorate is heated to a temperature a little above its melting-point—

$$2KClO_3 = KClO_4 + KCl + O_2$$

Both perchloric acid and the perchlorates are made, also, by electrolysing chloric acid and solutions of chlorates Perchloric acid is a colourless liquid which has very marked oxidising properties It boils at about 138° C without decomposition When perchloric acid is treated with phosphorus pentoxide, a very powerful dehydrating agent, and distilled, the heptoxide of chlorine, Cl_2O_7, is obtained This is the anhydride of perchloric acid—

$$Cl_2O_7 + H_2O = 2HClO_4$$

The perchlorates are more stable than the chlorates They are not decomposed by hydrochloric acid, nor do they, like the chlorates, give off explosive gases when heated with sulphuric acid. They are not reduced to chlorides by sulphur dioxide Perchloric acid is used for these reasons as an assistant in the Kjeldahl process

CHAPTER XXVI.

THE NON-CHLORINATED OXIDISING BLEACHING AGENTS.

Hydrogen Peroxide, H_2O_2, is a bleaching agent of great value It is both powerful in its action and capable of being controlled easily It can be used for bleaching every known textile fibre without danger of tendering Hydrogen peroxide is present in small quantities in the atmosphere It is produced by the action of the ultra-violet rays on moisture, hydrogen being also formed—

$$2H_2O=H_2O_2+H_2.$$

It is also produced by the action of a silent electric discharge upon moist air, and by the natural oxidation of many organic and inorganic substances For example, when zinc is treated with sulphuric acid in the presence of air, hydrogen peroxide is produced as well as hydrogen—

$$Zn+2H_2O+O_2=Zn(OH)_2+H_2O_2.$$

Preparation of Hydrogen Peroxide.—Hydrogen peroxide is prepared by treating certain metallic peroxides with a dilute acid

The metallic peroxides are of two kinds

1 Those which are decomposed by cold dilute mineral acids yielding hydrogen peroxide as one product This class includes the peroxides of sodium, calcium, and barium When treated with sulphuric acid they react thus

$$Na_2O_2+H_2SO_4=Na_2SO_4+H_2O_2,$$
$$BaO_2+H_2SO_4=BaSO_4+H_2O_2.$$

2 Peroxides which are not decomposed by dilute cold acids but dissolve when the acid is heated, giving oxygen. Manganese dioxide is an example—

$$MnO_2+H_2SO_4=MnSO_4+H_2O+O.$$

Commercial hydrogen peroxide is made, generally, from barium peroxide, BaO_2 When barium oxide, BaO, is heated in a current of air to a temperature of 450° C it absorbs oxygen, giving the peroxide—

$$BaO+O\rightleftharpoons BaO_2.$$

This reaction is reversible at a higher temperature. At 800° C. the peroxide is decomposed into barium oxide and oxygen. The reaction can be controlled by altering the pressure. If barium oxide be treated with oxygen under a high pressure, peroxide is formed. If the pressure be then reduced greatly (to nearly a vacuum) the oxygen is given off at the same temperature This is the basis of Brin's method for the manufacture of oxygen.

Barium peroxide is a white powder which is insoluble in water. It may be

made, also, by treating a solution of barium oxide in water with hydrogen peroxide, when crystalline barium peroxide, $BaO_2.8H_2O$, is thrown down. This, when heated to 130° C, loses its water, becoming anhydrous and amorphous. When heated more strongly, as noted above, it is transformed into the monoxide, oxygen being evolved.

Hydrogen peroxide may be made from barium peroxide by grinding the latter to a cream with water and stirring this into a slight excess of cold dilute sulphuric acid. Other acids, such as phosphoric acid or hydrosilicofluoric acid, are also used—

$$BaO_2+H_2SO_4=BaSO_4+H_2O_2,$$
$$3BaO_2+2H_3PO_4=Ba_3(PO_4)_2+3H_2O_2,$$
$$BaO_2+H_2SiF_6=BaSiF_6+H_2O_2.$$

After completion of the reaction, the excess of sulphuric acid is precipitated by adding barium carbonate, and the solution of hydrogen peroxide filtered off.

Another method is to use carbon dioxide instead of a mineral acid. The barium peroxide is stirred into water, cooled by means of ice, through which a current of carbon dioxide is passed Barium carbonate is precipitated and hydrogen peroxide remains in the solution—

$$BaO_2+CO_2+H_2O=BaCO_3+H_2O_2.$$

Excess of carbon dioxide must be avoided, since, if present, barium percarbonate, $BaCO_4$, may be formed.

The solutions obtained by these methods contain about 3 per cent. by weight of hydrogen peroxide. They cannot be concentrated at ordinary pressures, since hydrogen peroxide is decomposed into water and oxygen when heated But dilute aqueous solutions of hydrogen peroxide may be distilled in a vacuum without decomposition If a dilute solution of hydrogen peroxide be heated to a temperature of from 35° to 40° C., at a pressure of 15 mm, a mixture of the peroxide and water distils over at first. If the temperature be raised gradually to 70° C. the residue in the distilling flask consists chiefly of peroxide This can be further concentrated by freezing it in liquid carbon dioxide and separating the crystals which form By drying these in a vacuum, over sulphuric acid, pure hydrogen peroxide may be obtained.

But concentrated forms of hydrogen peroxide are more commonly prepared from sodium peroxide. If this body be treated with 20 per cent. sulphuric acid at a low temperature, the sodium sulphate which is produced is more than is required to saturate the solution, and part of it crystallises out. Owing to the water of crystallisation it contains $Na_2SO_4.10H_2O$, the solution is, at the same time, concentrated. After removing the crystals of sodium sulphate the solution is concentrated *in vacuo* at a low temperature and then frozen.

Commercial hydrogen peroxide is a solution of the peroxide in water. There are three standard strengths, known as "ten- to twelve-volume," "twenty-volume," and "one-hundred-volume" hydrogen peroxide respectively.

When hydrogen peroxide decomposes it yields oxygen in accordance with the equation

$$H_2O_2=H_2O+O.$$

Ten-volume hydrogen peroxide means that the hydrogen peroxide present in any given volume gives, at 0° C. and 760 mm. pressure, ten times its volume of oxygen. The following table gives the composition of these solutions:—

	Grammes of Hydrogen Peroxide, H_2O_2, in 100 c c of the Solution	Volume of Oxygen at 0° C and 760 mm Pressure given by 100 c.c. of the Solution.
10-volume peroxide .	3 0	10×100 c c
20-volume ,, .	6 0	20×100 c c
100-volume ,, . (Also known as perhydrol.)	30·0	100×100 c.c.

From the equation given above it is seen that 34 grammes of hydrogen peroxide yield 16 of oxygen

According to Avogadro's law, 16 grammes of oxygen occupy 11·2 litres when measured at 0° C. and 760 mm. pressure. Hence 3 grammes of oxygen will measure $\frac{11{\cdot}2\times3}{34}$, or 990 c.c

Thus, if 100 c c. of ten-volume peroxide contain 3 grammes of hydrogen peroxide, H_2O_2, the oxygen given by this volume of the solution will occupy 990 or approximately 1000 c c , i.e. *ten times* the volume of the solution Similarly, the oxygen yielded by any volume of one-hundred-volume peroxide will be 100 times the volume of the solution taken.

Properties of Hydrogen Peroxide.—Pure hydrogen peroxide is a colourless, viscous liquid, which has no smell. It burns the skin and produces blisters. When heated at ordinary pressure it is decomposed into water and oxygen, but it can be distilled without decomposition in a vacuum. Its boiling-point at 26 mm pressure is 84° to 85° C It solidifies when cooled to —2° C.

Hydrogen peroxide is soluble in water in all proportions. Its aqueous solution has a slightly acid or bitter taste, and a faintly acid reaction towards litmus

An aqueous solution of hydrogen peroxide is fairly stable in the presence of a small quantity of an acid Sulphuric acid, or phosphoric acid, is commonly added to commercial solutions to render them stable According to Maass and Hiebert (*J Soc Dyers and Col*, 1924, p. 116), hydrogen fluoride acts as a stabiliser, whilst other halogen acids decompose hydrogen peroxide at all concentrations. For hydrochloric acid there is a critical concentration, below which the rate of *decomposition is monomolecular, and above which chlorine is liberated and* swept out of the reaction mixture by the liberated oxygen. The rate constant is proportional, probably, to $(1-\alpha)\times$(acid concentration), where α is the dissociation of the acid. The mechanism of the reaction is, possibly, the formation of the complex H_2O_2 HCl, which breaks down into hypochlorous acid and water, followed by reaction between the hypochlorous acid and the peroxide. Above the critical concentration the liberation of chlorine is due to displacement of the equilibrium of the system, hypochlorous acid, acid hydrochloric, and acid chlorine. With hydrobromic acid the reaction is analogous, but the rate is greater than with hydrochloric acid, and the bromine is liberated at a lower concentration. Hydrolysis of the halogens, with formation of oxy-acids, causes decomposition of the peroxide, accompanied by the formation of halogen acid. When an acid, or neutral solution, of hydrogen peroxide is heated the peroxide is decomposed, the rate of decomposition rising with the temperature If the solution be made alkaline with ammonia or sodium hydroxide, the loss of oxygen becomes much more rapid at any temperature. Weber (*J. Soc. Dyers and Col.*, 1923, p. 212)

found that if 0·5 c c. of 0 897 sp gr ammonia were added to 500 c.c. of one-volume hydrogen peroxide the loss at 100° F. in three hours was about 20 per cent of the hydrogen peroxide present The same volume of one-volume peroxide to which no ammonia was added lost nothing during the same time. With more ammonia the oxygen was given up more freely, and with ten times the amount used above, the loss was 69·70 per cent. of the total hydrogen peroxide present. That is, faintly alkaline solutions are more stable than those containing more alkali.

The rate of decomposition was much slower when the solution was neutralised with sodium silicate (*vide* p 509)

Metals or their oxides, or particles of dirt, all render solutions of hydrogen peroxide unstable and cause the liberation of oxygen, the metallic oxide playing the part of a catalytic agent. Copper and iron and manganese are particularly active in this respect, while lead is one of the least active. Hydrogen peroxide cannot be kept in metal vessels, and if a bleaching vessel is made of metal, lead is the only one permissible. The action of metals on solutions of hydrogen peroxide can be illustrated by introducing platinised asbestos, when bubbles of oxygen will immediately appear. Dirt acts, probably, as a catalytic agent because it contains metallic oxides But even rough though clean surfaces of inert substances, such as glass, appear to promote decomposition. According to Haller and Munk, if cotton be immersed in 30 per cent peroxide and a little oxide of iron or cobalt be added, very rapid decomposition, accompanied by destruction of the fibre, occurs.

Hydrogen Peroxide as an Oxidising Agent.

Since hydrogen peroxide, like ozone, contains an atom of loosely combined oxygen, it has powerful oxidising properties. It owes its bleaching action, also, to the same cause The following are examples of its oxidising properties —

1. It liberates iodine from potassium iodide—

$$2KI+H_2O_2=2KOH+2I.$$

The reaction is more delicate in the presence of some dilute acid to neutralise the potassium hydroxide

2 Like ozone, hydrogen peroxide oxidises lead sulphide to sulphate—

$$PbS+4H_2O_2=PbSO_4+4H_2O$$

3 It oxidises sulphurous acid, or sulphites, to sulphuric acid and sulphates—

$$H_2SO_3+H_2O_2=H_2SO_4+H_2O.$$

4 It oxidises ferrous to ferric salts—

$$2FeSO_4+H_2SO_4+H_2O_2=Fe_2(SO_4)_3+2H_2O.$$

5. It bleaches litmus and many colouring matters.

Hydrogen Peroxide as a Reducing Agent.—When hydrogen peroxide reacts with another body which also contains an atom of loosely combined oxygen, it behaves as a reducing agent in the same way as ozone, oxygen being evolved Thus ·

1. Silver oxide is reduced to metallic silver—

$$Ag_2O+H_2O_2=Ag_2+H_2O+O_2.$$

2. Freshly precipitated manganese dioxide and sesquioxide in the presence of dilute sulphuric acid are first reduced to manganous oxide and then dissolved as manganous sulphate—

$$(1)\ MnO_2+H_2O_2=MnO+H_2O+O_2$$
$$(2)\ MnO+H_2SO_4=MnSO_4+H_2O$$

3. Ozone is reduced by hydrogen peroxide to oxygen—

$$O_3+H_2O_2=H_2O+2O_2.$$

4. Potassium permanganate in the presence of dilute sulphuric acid is reduced to colourless soluble manganese sulphate—

$$2KMnO_4+5H_2O_2+3H_2SO_4=2MnSO_4+K_2SO_4+8H_2O+5O_2.$$

This reaction is of importance in the estimation of hydrogen peroxide It takes place in the following manner Potassium permanganate is a compound of potassium oxide with manganese heptoxide, thus, $K_2O\ Mn_2O_7$ Manganese heptoxide contains five atoms of loosely combined oxygen—

$$Mn_2O_7=2MnO+5O.$$

In presence of hydrogen peroxide the following reactions take place —

$$(1)\ K_2O\ Mn_2O_7 \quad =K_2O+2MnO+5O$$
$$(2)\ K_2O+H_2SO_4 \quad =K_2SO_4+H_2O.$$
$$(3)\ 2MnO+2H_2SO_4=2MnSO_4+2H_2O.$$
$$(4)\ 5O+5H_2O_2 \quad =5O_2+5H_2O.$$

5 Chlorine, when treated with hydrogen peroxide, is changed into hydrochloric acid, and oxygen is liberated—

$$Cl_2+H_2O_2=2HCl+O_2.$$

The Acid Properties of Hydrogen Peroxide.— Hydrogen peroxide contains two atoms of hydrogen which can be displaced by a metal, giving two classes of substitution products In the case of sodium these are—

$$(1)\ NaO_2H$$
$$(2)\ NaO_2Na$$

The monosubstitution compounds are termed hydroperoxides They are formed when the hydroxide of calcium, magnesium, or barium is treated with excess of hydrogen peroxide—

$$Mg(OH)_2+2H_2O_2=MgH_2O_4+2H_2O$$

These hydroperoxides are comparatively stable compounds They are represented, sometimes, as addition compounds, *e g.* $MgO_2\ H_2O_2$ They are of importance in bleaching since, when heated with water, they only give up their oxygen very slowly, even at the boiling-point—

$$MgH_2O_4=Mg(OH)_2+O_2$$

When a solution of hydrogen peroxide is treated with sodium carbonate it acts like an acid, exchanging its hydrogen atoms for sodium and liberating carbonic acid—

$$H_2O_2+Na_2CO_3=Na_2O_2+H_2CO_3.$$

The Constitution of Hydrogen Peroxide.—Three different formulæ have been proposed for hydrogen peroxide, viz —

(1) H—O—O—H.

(2) $\begin{matrix} H \\ \diagdown \\ \diagup \\ H \end{matrix}$>O=O

(3) H—O=O—H

According to Stewart (*Recent Advances in Physical and Inorganic Chemistry*) the first of these, which is also the oldest, does not explain the presence of a comparatively loosely combined atom of oxygen together with a second which is more firmly combined. The second formula does explain this difference, while the third is more in agreement with certain other physical properties of the compound.

The Detection and Estimation of Hydrogen Peroxide.—The presence of hydrogen peroxide in a solution may be identified by the following tests —

1 Its reaction with potassium iodide

2 Its reaction with titanium salts Hydrogen peroxide gives an orange-yellow colour with a solution of a titanium salt According to Knecht, if a solution of titanous chloride be added to a solution of hydrogen peroxide it is oxidised to the state of TiO_3 if excess of hydrogen peroxide be present This is accompanied by the production of a yellow or orange yellow colour—

$$H_2O_2+TiO_2=H_2O+TiO_3$$

By continuing the addition of the titanous chloride solution the colour will either increase or decrease in intensity according to the amount of peroxide present, but by continued addition it will disappear altogether in accordance with the equation

$$TiO_3+2TiCl_3+6HCl=3TiCl_4+3H_2O$$

3 The chromic acid reaction This is very delicate A drop or two of a solution of potassium bichromate and some dilute sulphuric acid are added to some of the peroxide solution in a test tube About 5 c c of ether are then added the test tube closed, and shaken In the presence of hydrogen peroxide the ether is coloured blue This is thought to be due to the formation of a compound of perchromic acid, $HCrO_4$, with hydrogen peroxide

The Estimation of Hydrogen Peroxide.—Either the oxygen may be liberated and measured, or the peroxide may be titrated with a standard solution of potassium permanganate

The latter method is more convenient Ten c c of ten volume peroxide are diluted to 100 c c in a stoppered flask Ten c c of this mixture (*i e* 1 c c of the original solution) are placed in a beaker or flask and diluted to about 300 c c with distilled water, after which from 20 to 30 c c of sulphuric acid (1 in 4) are added Decinormal potassium permanganate solution is then run in from a burette, with constant agitation of the mixture, until a permanent pink colour is produced If at first the colour of the permanganate does not disappear, or if a brownish tint is produced, more sulphuric acid should be added The hydrogen peroxide may now be calculated either by weight or by volume Each cubic centimetre of decinormal permanganate corresponds to 0 0017 gramme of hydrogen peroxide (see equation given above)

If the result be required in volumes of oxygen, it is known that 3·04 grammes

of hydrogen peroxide give 1000 c.c. of oxygen. Hence 1 gramme of hydrogen peroxide gives 329 c.c.

Titration by Means of Iodine.—The hydrogen peroxide is diluted with water until it contains about 0·6 per cent by weight. Two grammes of potassium iodide dissolved in 200 c.c. of water in a flask and 30 c.c. of sulphuric acid (1 in 2) are added. After cooling the mixture, 10 c.c. of the diluted peroxide solution are introduced by means of a pipette and the flask allowed to stand for a short time. The reaction is

$$H_2O_2+2KI+H_2SO_4=K_2SO_4+2H_2O+I_2.$$

The iodine is then titrated by means of decinormal thiosulphate solution. From the equation it is evident that 34 grammes of hydrogen peroxide liberate 254 grammes of iodine, *i.e.* each cubic centimetre of decinormal thiosulphate corresponds to 0·0017 grammes of hydrogen peroxide

This method is sometimes preferable to the permanganate titration, because peroxide solutions may contain other bodies than hydrogen peroxide which are oxidised by potassium permanganate.

The Direct Measurement of the Volume of Oxygen produced.—A nitrometer (fig 173) is filled with mercury and connected, by means of a piece of pressure tubing, with a small decomposition flask. In the outer compartment of this are placed some potassium permanganate solution and dilute sulphuric acid, and in the inner tube 1 c.c of the peroxide solution The flask is then allowed to cool to the room temperature and connected with the nitrometer, as shown in the illustration The three-way tap is then opened carefully, and the open tube of the nitrometer is moved until the air in the decomposition flask is at atmospheric pressure. The level of the mercury in the graduated tube is then read off. The nitrometer tube is now connected with the decomposition flask by means of the three-way tap The open tube is then lowered to reduce the pressure and the decomposition flask is tilted to bring the peroxide into contact with the acid permanganate After the oxygen has been liberated and allowed to cool to the temperature of the atmosphere, the open tube is again adjusted till the level of the mercury is the same as in the other, and the volume of gas read off. The increase in volume is due to the oxygen liberated from the peroxide and permanganate, half of it coming from the peroxide. This should now be reduced to 0° C. and 760 mm pressure by means of the formula

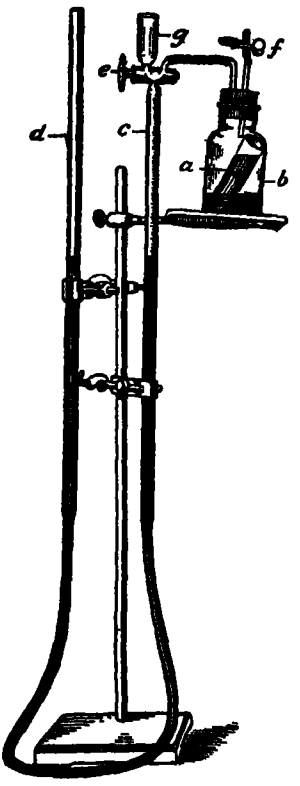


Fig. 173.—Nitrometer for hydrogen peroxide

$$\frac{VP}{273}=\frac{V'P'}{273+t'}.$$

The Use of Hydrogen Peroxide in Bleaching.—The bleaching-vat should be constructed of hard white wood, slate, or glazed bricks, and made in such a way that no metal can come in contact with the bleaching liquor. Lead is the

only metal which it is safe to use, but it becomes coated with lead peroxide, which may cause lead stains on the bleached goods Where a lead steam pipe is used for heating the liquor, it should be placed beneath a false perforated bottom to prevent the goods from coming into contact with it The vat should be well soaked with a peroxide solution before use The Castner-Kellner Alkali Co. recommend a vat of the nature shown in fig 174 as being satisfactory for most purposes. It is heated by means of a lead steam coil placed beneath a false bottom, entering at one end, coiling backwards and forwards, and finally going out at the other end of the vat An open steam pipe should never be used The false bottom above the steam pipe prevents the goods from becoming entangled with the pipe, and allows any suspended solid matter in the liquor to settle out. A movable perforated top is provided, which can be fixed just beneath the surface of the liquor, thus ensuring that the goods are completely covered by the bleaching liquor

For piece goods, a suitable jigger or washing-machine may be used, provided

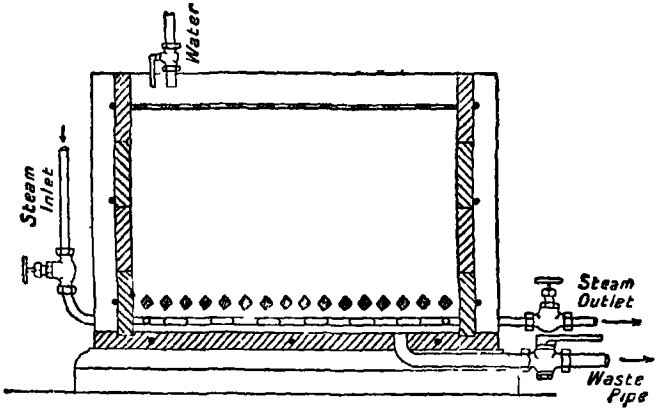


FIG 174.—Castner-Kellner bleaching-vat.

that there are no metal parts which can come into contact with the hydrogen peroxide, while, for small lots, a glazed pan into which steam can be blown is suitable. New apparatus should always be treated alone with the bleaching solution before being used for goods

The strength of the bleaching-bath varies with the nature of the material As a rule, a solution containing about 0·5 per cent (*i e.* 5 grammes per litre) of hydrogen peroxide is sufficiently concentrated Weber (*loc cit*) recommends a standard bath of two-volume peroxide. It is a disadvantage to have the solution too concentrated, since it not only loses peroxide more quickly than a dilute one, but may cause over-bleaching With regard to the volume of liquor, as a rule from fifteen to twenty times the weight of the goods is required for an ordinary bath, but less is necessary if a jigger is used

Preparation of the Bleaching-bath.—Water is first placed in the bath and the necessary volume of peroxide is added. As a rule, this solution will have an acid reaction. It has been mentioned above that acid solutions of peroxide are comparatively stable. In fact they are so stable as to be unsuitable for bleaching Hence, the bath must be made faintly alkaline But only a mild alkali can be used If sodium hydroxide were employed the cotton would be tendered, since in its presence oxygen converts cellulose into oxycellulose.

The alkalis used are (1) ammonia, (2) sodium silicate, (3) sodium phosphate. Either ammonia or sodium silicate is generally employed, a dilute solution being stirred in until the reaction of the bath is very faintly alkaline to litmus. Weber (*J. Soc. Dyers and Col.*, 1923, p 212) recommends phenol red as a more suitable indicator. It is very sensitive, and has a sharp colour change from yellow to red. He found, also, that when ammonia is used for neutralising the bath there is a considerable loss of bleaching power owing to decomposition of the peroxide, and that this loss increases with the quantity

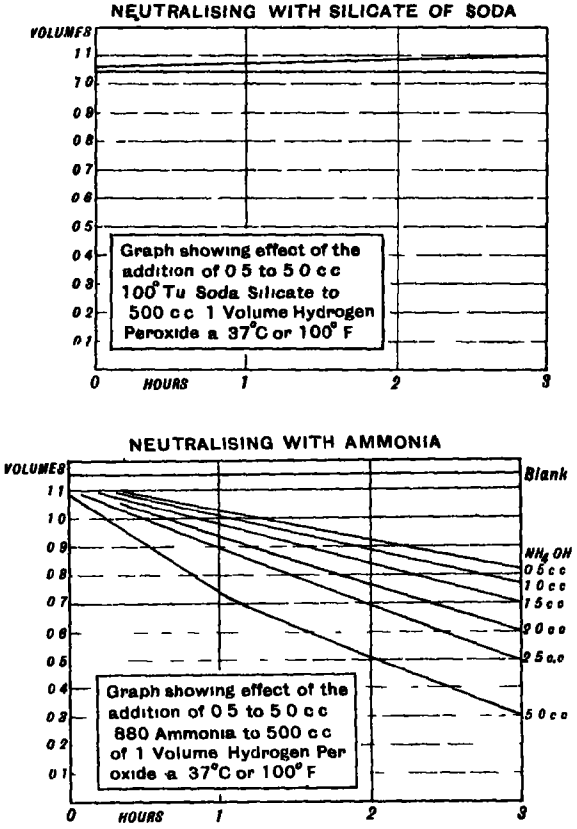


FIG. 175.—Effect of alkali on hydrogen peroxide.

of ammonia present. This emphasises the necessity for careful neutralisation and the use of a delicate indicator Phenol red has a pH range of from 6·8 to 8·4. These experiments have been referred to above. But using sodium silicate under the same conditions the loss was negligible. This is illustrated by the graphs (fig. 175) taken from Weber's paper.

The only objection to sodium silicate is that, if too much be used, the goods may acquire a harsh feel But Weber states that if 1 lb is used for every 20 gallons of ten- to twelve-volume peroxide there is no danger of this happening. He gives the following directions for making a 240 gallon standing-bath Forty gallons of twelve-volume peroxide are added to 200 gallons of water and

neutralised by the addition of 2 lbs. of sodium silicate dissolved in half a gallon of hot water.

Temperature of the Bleaching-bath.—The best temperature for bleaching with hydrogen peroxide is 100° F. (40° C.) Above 40° C. hydrogen peroxide is lost rapidly, and at lower temperatures its bleaching action is only developed slowly

The Use of Assistants.—Various bodies are used either with the object of assisting penetration of the bleaching liquor or controlling the rate of evolution of oxygen.

Soap is sometimes added, since it increases the wetting or penetrating power of the liquor. From 1 to 3 lbs per 100 gallons is a suitable quantity. The soap chosen must, of course, be readily soluble in water at the temperature of the bath. A pure olive-oil soap or turkey-red oil is most suitable. It should be remembered that if the goods have been completely scoured they will be perfectly permeable, while, if not, soap will not remedy the defect, and patchy bleaching is in any case probable.

Stabilising Agents.—The difficulties associated with peroxide bleaching may be inferred from what has been said already But they may be summarised briefly. They are—

1. Acid or neutral solutions are not sufficiently active.
2. Alkaline solutions are liable to lose peroxide too rapidly to exercise their full bleaching effect
3. Particles of dirt, suspended mineral matter, metals or their oxides act as catalysts, causing rapid decomposition of the peroxide
4. The bleaching action is developed best in a warm bath, but instability varies inversely with the temperature.

Stabilising agents are used in order to prevent too rapid decomposition of the hydrogen peroxide under the conditions of the bleaching-bath. The more important are—

1. *Colloids.*—The stabilising effect of sodium silicate has been referred to already It performs a dual function in the bath, both neutralising the free acid and, on account of its colloidal nature, acting as a stabilising agent. Soap, also a colloid, acts as a stabiliser and is used sometimes for this purpose Other colloidal bodies, such as glue, could be used equally well

2. Wolfenstein (*J S.C.I.*, 1907, p. 1275) patented the use of salts of an acid stronger than carbonic acid and having an alkaline reaction to litmus, such as those of phosphoric acid. Both ammonium and sodium phosphates are used commonly as stabilisers. From $\frac{1}{4}$ to 1 lb. per 100 gallons is sufficient

3 But the most important stabiliser is magnesia, MgO This acts, as stated above, by forming magnesium hydroperoxide. Baths containing this compound may be used even at the boiling-point. The quantity of magnesium oxide required is about the same as the weight of hydrogen peroxide present in the bath, *i.e.* 10 gallons of ten-volume peroxide would require about 3 lbs Whenever magnesia is used the bleached goods must always be soaked in a bath of dilute acid before washing.

The Bleaching Process.—Only soft, or softened, water should be used in preparing the bleaching-bath. It must be free from suspended matter or dissolved organic impurities. It is very important, also, that the goods should be thoroughly scoured before bleaching. Calcium and magnesium soaps, in particular, should be absent, since they inhibit penetration of the liquor.

The bath is heated to a temperature of about 100° F. The scoured goods are hydro-extracted and passed into the bath The steam is then turned on until the temperature reaches 100° F. The goods are generally worked in the bath at this temperature for about three hours, after which they are left in the bath for some hours and allowed to cool off. Circulation is very important. Heavy goods often become pressed together and incompletely bleached in consequence. In the case of piece goods some form of mechanical circulation should be provided, but it must not be forgotten that agitation of the liquor increases its rate of decomposition The strength of the liquor and its reaction should be tested from time to time and adjusted if necessary If the goods are left in the liquor, they should be kept completely immersed by means of the perforated lid, but sometimes, after the preliminary working, they are taken out of the bath and exposed to the air to complete the bleaching action

After bleaching the goods are wrung out, the peroxide liquor being returned to the bath, and well washed with soft water A preliminary bath of sulphuric acid (1° to 2° Tw.) is, however, often used before washing, as it helps to clear them. After washing they are hydro-extracted and dried

The cost of peroxide bleaching can be reduced by combining it with treatment with sulphurous acid or potassium permanganate. If sulphurous acid be employed, the goods from the peroxide bath are washed with water, soaked in a solution of sulphur dioxide in water or acidified sodium bisulphite for two or three hours and then washed again If the peroxide and permanganate bleach be used, treatment with the latter comes first This process will be described later

The used peroxide liquor is tested by one of the methods described and made up to the correct concentration for the next lot of goods

Sodium Peroxide, Na_2O_2.—This body is formed when dry carbon dioxide free air is passed over metallic sodium heated to a temperature of 300° C Pure sodium peroxide is a white powder, but the commercial peroxide is yellowish in colour, containing from 95 to 98 per cent. of sodium peroxide, Na_2O_2 A crystalline product, $Na_2O_2\ 8H_2O$, is also known

Sodium peroxide is stable if kept in a closed vessel at a low temperature and free from moisture, but when heated it gives up oxygen in accordance with the equation

$$Na_2O_2 = Na_2O + O$$

It thus contains about 20·5 per cent of "available" oxygen, and is a very powerful oxidising and bleaching agent If left in contact with inflammable organic substances, such as wool or cotton, the heat evolved by the oxidation is sufficient to ignite the material. Sodium peroxide dissolves in water, but is at the same time decomposed When it is treated with cold water, hydrogen peroxide and sodium hydroxide are formed and much heat is developed—

$$Na_2O_2 + 2H_2O = H_2O_2 + 2NaOH.$$

If, however, hot water be used, the hydrogen peroxide is decomposed and oxygen is evolved

When treated with cold dilute solutions of acids, sodium peroxide yields hydrogen peroxide and the sodium salt of the acid used—

$$Na_2O_2 + H_2SO_4 = H_2O_2 + Na_2SO_4.$$

It is obvious, therefore, that a solution of sodium peroxide has the same properties as one of hydrogen peroxide, and that the dry sodium peroxide may

be regarded as a convenient source of the latter. It is sold in air-tight drums, and so long as these are kept air-tight no deterioration occurs. But when sodium peroxide is exposed to air it is attacked quickly by atmospheric moisture and the hydrogen peroxide thus formed is lost

The Castner-Kellner Alkali Co., Ltd., who manufacture sodium peroxide, claim the following advantages over hydrogen peroxide (1) It is perfectly stable if kept properly (2) It requires less room than its equivalent volume of hydrogen peroxide. (3) There are no glass carboys to be broken. (4) The shaking incidental to transit does not affect sodium peroxide but increases the tendency of hydrogen peroxide to decompose.

The Equivalent Values of Sodium Peroxide and Hydrogen Peroxide.—From the equation

$$Na_2O_2+H_2O=2NaOH+H_2O_2$$

it is seen that 78 parts by weight of sodium peroxide yield 34 of hydrogen peroxide

Hence, 1 part of hydrogen peroxide requires 2·29 parts of sodium peroxide.

Now, ten-volume peroxide contains 3 per cent. by weight of hydrogen peroxide That is, 10 gallons contain 3 lbs To produce this, $3\times2\cdot29$, *i.e.* 6·87 lbs of sodium peroxide, would be required Hence, 6·87 lbs of sodium peroxide dissolved in 10 gallons of water give approximately a ten-volume solution Or, according to the Castner-Kellner Co, one case containing 240 lbs of sodium peroxide will make 290 gallons of ten- to twelve-volume peroxide

Preparation of Bleaching Solutions.—An aqueous solution of sodium peroxide cannot be used for bleaching, since it contains sodium hydroxide This would damage wool and silk rapidly, and cause also tendering, due to oxycellulose, if used with hydrogen peroxide for bleaching cotton

The sodium hydroxide must be replaced by a milder alkali, such as ammonia or sodium silicate This is usually done in the following manner:—

Before dissolving the sodium peroxide, sufficient sulphuric or hydrochloric acid is added to the water to completely neutralise the sodium hydroxide produced and leave the bath faintly acid.

From the equation

$$Na_2O_2+H_2SO_4=Na_2SO_4+H_2O_2$$

it is seen that 78 parts of sodium peroxide require 98 of sulphuric acid. Hence, for each pound of sodium peroxide used, 1·26 lbs. of sulphuric acid are necessary. If the acid is 96 per cent strength, the quantity would be $\frac{1\cdot26}{96}\times100$, or 1·32 lbs. A little more than the theoretical quantity is used. Having mixed it with the water in the bath and allowed the mixture to cool, the weighed sodium peroxide is then scattered over the surface of the liquid and stirred in. When the sodium peroxide has dissolved completely the solution is tested with litmus paper. If it be not acid, insufficient sulphuric acid was used and sodium hydroxide is present. More dilute sulphuric acid must now be stirred in till the reaction of the bath is distinctly acid to litmus But, as with hydrogen peroxide, the bleaching-bath must be faintly alkaline. Dilute ammonia solution is stirred in carefully, little by little, till the reaction of the bath is just alkaline to phenol red

The bath is now ready for use. Sodium silicate may be used instead of ammonia if preferred, and also any of the assistants mentioned in connection with hydrogen peroxide.

The water used for making up the bath should be soft or softened, free from suspended matter, organic matter, and iron. The acid used should be iron free

also Hydrochloric acid, if it does not contain iron, has some advantages over sulphuric acid It evolves much less heat than sulphuric acid when mixed with water, and also in the decomposition of the sodium peroxide

The quantity of hydrochloric acid required is found thus

$$Na_2O_2+2HCl=2NaCl+H_2O_2,$$

i e 78 parts of sodium peroxide require 73 of acid, or 1 part of sodium peroxide requires 0 936 of acid

If hydrochloric acid of 30° Tw is used, this contains 30 0 per cent of real hydrochloric acid Hence, the quantity required for each part of sodium peroxide becomes $\frac{0\,936\times 100}{30}$, or 3 12

Magnesium sulphate may be employed instead of acid to decompose the sodium peroxide, giving a bath containing magnesium hydroperoxide which, as mentioned above has considerable stability, and is useful for goods which are difficult to bleach or require a higher temperature than usual

The reactions are —

$$Na_2O_2+H_2O=H_2O_2+2NaOH,$$
$$2NaOH+MgSO_4=Mg(OH)_2+Na_2SO_4$$

The sodium hydroxide is thus replaced by insoluble and therefore harmless magnesium hydroxide a turbid bath containing magnesium hydroperoxide being produced Magnesium sulphate is used as crystalline Epsom salt, $MgSO_4\,7H_2O$ For each pound of sodium peroxide used, 3 2 lbs of Epsom salt are required This is first dissolved in water in the bath and the sodium peroxide is stirred in gradually

After the bath is made up, it is advisable to let it stand for a short time and skim off any scum which rises to the surface The strength of the bath varies with the material to be bleached, but from 10 to 15 lbs of sodium peroxide to each 100 gallons of bleaching liquor is generally sufficient

The bleaching vessel is of the same kind as used for hydrogen peroxide, and the temperature and duration of bleaching are also the same After bleaching, the goods are washed with water but, as with hydrogen peroxide it is advantageous to give them a preliminary bath of dilute acid (*e g* 1° Tw hydrochloric acid)

Certain points in connection with the use of sodium peroxide are emphasised by the Castner Kellner Co When handling sodium peroxide in powder form, as, for instance, when weighing it out to prepare a bleaching liquor, a scoop made of tinned or enamelled iron should be used Peroxide must never be weighed on scale pans Any traces of iron or copper which might be obtained from metal pans would act as a catalytic agent in the bleaching bath A special vessel made of glass, earthenware, or enamelled iron should be kept for the purpose Scoops must be perfectly clean and dry After using they should be washed at once with water and dried carefully

A separate dissolving tank for making the sodium peroxide solution has some advantages It enables a strong stock solution to be prepared from which several bleaching tanks can be served A round wood tank built up like the top half of a barrel, fitted with a mechanical wooden stirrer, is recommended It should have two run off cocks of wood, one 2 to 3 inches above the bottom, for the bleaching liquor, and the other at the bottom for running off the waste The floor of the tank should slope distinctly towards this waste cock

A few examples of sodium peroxide bleaching-baths may be noted

For fine cotton goods and laces the Castner-Kellner Alkali Co. recommend the following bath —

100 gallons of water,
10½ lbs. sulphuric acid of 168° Tw.,
8 lbs sodium peroxide,
¼ lb sodium phosphate.

Before introducing the goods, sufficient ammonia is added to produce a slight alkalinity to litmus paper The bath is gradually heated to 50° C., when the goods are entered and treated as already described.

It is now unnecessary to use sodium phosphate, since all the peroxide made by this firm for bleaching purposes contains this substance

Koechlin (*J S C I.*, 1899, p 1119) employs the following method for cotton goods. They are boiled for six hours at a pressure of two-thirds of an atmosphere in a liquor containing 10 kg of dry caustic soda, 10 kg of soap, 1 kg of calcined magnesia, and 30 litres of hydrogen peroxide to 1000 litres of water They are then washed, soured, again washed and dried The white produced is said to be better than that obtainable with hypochlorites

Mohr's bleaching process (*J Soc Dyers and Col.*, 1924, p 23) is said to dispense with the necessity of lye boiling The process is as follows —

1 Immediately after singeing, the fabric is passed through a Foulard machine containing an old bath from the oxygen bleach (3) It is then passed, in rope form, into wooden vats in which it remains for about forty-eight hours

2 When the goods are completely softened, they are run through a washing machine and then into a lead-lined iron bleaching kier A special mechanism ensures that the goods are impregnated with a bleaching-powder solution and automatically arranged in the kier, which is closed and kept under pressure for from one to two hours The goods are then rinsed, acidified, and rinsed again

3 A solution of sodium peroxide is then pumped on to the goods in the kier and allowed to act on them for three to four hours at 60° C After pumping off this liquor the kier is opened and the goods run without rinsing into a washing machine containing a weak soap solution from which they pass to another containing pure water

Analysis of Sodium Peroxide.— A weighed quantity of the powder is dissolved in a slight excess of dilute sulphuric acid and the solution made up to a definite volume This is then tested by any of the methods described for hydrogen peroxide Bleaching liquors are also tested in the same way

The Per-acid Bleaching Agents.

This name is given to derivatives of acids derived from hydrogen peroxide by substituting an acid radicle for one or more of the hydrogen atoms. The class includes perboric, persulphuric, and percarbonic acids, all of which are used as bleaching agents

If hydrogen peroxide be represented by the formula H—O—O—H, and boric acid by the formula O B—OH, then perboric acid is O=B—O—OH

Similarly, the relationship between sulphuric acid and persulphuric acid is—

Sulphuric acid, HO SO_2 OH ; persulphuric acid, HO.SO_2.O—O—H

The term peracid has sometimes another meaning, as in the case of perchloric acid, $HClO_4$, or permanganic acid, $HMnO_4$. In these cases it signifies that the acid-forming oxide exists in the highest known state of oxidation. Thus,

permanganic acid is derived from the keptoxide of manganese, Mn_2O_7, in which manganese exists in its most highly oxidised condition—

$$Mn_2O_7+H_2O=2HMnO_4$$

The salts of these per-acids are also bleaching agents, but they act, as a rule, in a different manner They tend to give nascent oxygen directly when decomposed, while the true per-acids give in the first instance hydrogen peroxide, which breaks down subsequently into oxygen and water Fuller information may be found in Stewart's *Recent Advances in Physical and Inorganic Chemistry*, from which many of the facts given here are taken

Sodium perborate is an important bleaching and oxidising agent. It may be regarded, as indicated above, as the sodium salt of perboric acid, HBO_3. This acid has not, however, been prepared Sodium perborate may be prepared by treating solutions of borax or boric acid with hydrogen peroxide or sodium peroxide at a low temperature. The various methods are summarised by the following equations.—

(1) $2NaOH+Na_2B_4O_7\ 10H_2O+4H_2O_2+H_2O=4NaBO_3+16H_2O$
(2) $Na_2O_2+H_3BO_3+HCl+2H_2O \quad =NaBO_3\ 4H_2O+NaCl$
(3) $Na_2O_2+H_2O_2+2H_3BO_3 \quad =2NaBO_3\ 4H_2O$

The formula $NaBO_3\ 4H_2O$ is not undisputed Foerster (*J Soc. Dyers and Col*, 1921, p 251) regards it as $NaBO_2\ H_2O_2\ 3H_2O$. According to Jaubert (*J S C I*, 1904, p 1145), if 248 grammes of boric acid be mixed with 78 grammes of sodium peroxide and the mixture added gradually to 2 litres of cold water, a solution is obtained which subsequently throws down crystals which may be filtered off and dried at a low temperature. When titrated with potassium permanganate these crystals give up oxygen corresponding to the formula $Na_2B_4O_8\ 10H_2O$ If sufficient acid be added to the solution to neutralise half the sodium present, crystals of sodium perborate, $NaBO_3\ 4H_2O$, are obtained

Properties of Sodium Perborate.—Sodium perborate is a white crystalline substance which is quite stable if kept dry It is sparingly soluble in water. At 15° C 100 parts of water dissolve 1·93 of the salt. When sodium perborate is dissolved in water, heat is absorbed and the solution becomes colder It is more soluble in warm water, but at temperatures above 35° C the solution begins to decompose When sodium perborate is dissolved by water it is also decomposed into a mixture of hydrogen peroxide, borax, and sodium peroxide—

$$4NaBO_3+5H_2O=4H_2O_2+Na_2B_4O_7+2NaOH$$

Owing to its limited solubility, the hydrogen peroxide is produced very gradually, and its action is therefore easy to control If sufficient hydrochloric or sulphuric acid be added to neutralise the sodium hydroxide produced, a bleaching-bath containing hydrogen peroxide and borax is obtained.

Weaker acids, such as sodium bicarbonate, may be used for the same purpose Solutions of sodium perborate are rendered unstable, like those of hydrogen peroxide, by metals, such as iron, copper, or manganese, or by dirt.

The presence of borax in the solution makes it possible in some cases to scour and bleach at the same time, and perborates are used in this way for laundry work.

It will be seen from the equation given above that each molecule of sodium perborate, $NaBO_3.4H_2O$, yields one molecule of hydrogen peroxide or one atom of oxygen. This corresponds to 10·3 per cent. by weight, the available oxygen being about half that of sodium peroxide.

To prepare a bleaching-bath the perborate should be dissolved in warm water containing a slight excess of acid The solution is then made faintly alkaline in the same way as one made from hydrogen peroxide Cotton goods should not be put into a bath containing undissolved particles of perborate, since these may become deposited on the fabric and cause local over-bleaching. The bleaching is carried out in the same manner as with peroxide bleaches

According to de Keghel (*Les Products de Blanchement*, p 169) a solution of sodium perborate is completely decomposed at 68° C If, however, sodium pyrophosphate be added to the solution, the stability is increased greatly, complete decomposition only being brought about at the boiling-point This is due to the formation of a perpyrophosphate, to which de Keghel assigns the formula $(Na_4P_2O_9)_2 \frac{1}{2} H_2O$.

Persulphuric acid exists in two forms (1) permonosulphuric acid or Caro's acid, H_2SO_5, and (2) perdisulphuric acid, $H_2S_2O_8$ The mono- or Caro's acid is obtained by (1) the electrolysis of a fairly concentrated solution of sulphuric acid, (2) the action of concentrated sulphuric acid upon concentrated hydrogen peroxide, (3) as the potassium or ammonium salt by electrolysis of a saturated solution of potassium sulphate in dilute sulphuric acid

For the last method of preparation, the solution of the potassium or ammoniu[m] sulphate is placed in a platinum dish, which serves also as the anode. Into th[e] is dipped a porous pot containing dilute sulphuric acid and a platinum wi[re] cathode The surface of the cathode must be small for good results Th[e] platinum dish is cooled with water and a current of about 3 amperes is use[d] After a day or two potassium persulphate begins to crystallise out

Perdisulphuric acid can be prepared by treating cooled chlorosulphon[m] acid with hydrogen peroxide in accordance with the equation

$$2SO_2OHCl + H_2O_2 = 2HCl + H_2S_2O_8$$

The free acids are unstable In the presence of water they are changed, gradually, into sulphuric acid and oxygen, with hydrogen peroxide as an intermediate product This decomposition is shown by the equations

$$H_2S_2O_8 + H_2O = H_2SO_4 + H_2SO_5,$$
$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2,$$
$$H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2.$$

The persulphates are soluble in water According to Slater Price, the solubility of potassium persulphate, $K_2S_2O_8$, is less in solutions of potassium salts than in water and greater in solutions of sodium salts The increased solubility is due probably to the transformation of potassium into sodium persulphate The decomposition by water is represented by Slater Price as—

$$K_2S_2O_8 + H_2O = 2KHSO_4 + \tfrac{1}{2}O_2.$$

The reaction is unimolecular and is accelerated by acids The rate of liberation of oxygen is very slow at ordinary temperatures It commences at temperatures over 30° C, the rate increasing gradually with rising temperature up to 100° C The oxidising action of these compounds is on this account very easy to control

Examples of the oxidising action of persulphates are the liberation of iodine from potassium iodide, chlorine from chlorides, the oxidation of ferrous to ferric salts, and of manganese salts to permanganates. The reaction in the case of potassium iodide is

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$$

This reaction, and the liberation of chlorine from chlorides, is very sensitive to catalytic agents, such as salts of iron or copper. Iron salts are more active than those of copper, but acceleration is produced by mixing salts of both metals. According to Slater Price, silver salts act also as catalysts. Thus, a solution of potassium persulphate containing a small quantity of silver nitrate and acidified with nitric acid oxidises benzol to quinone, and then the quinone to maleic acid and carbon dioxide Oxalic acid is oxidised quantitatively to carbon dioxide. Similar reactions take place in the absence of silver nitrate, toluene being oxidised to benzaldehyde and benzoic acid

Persulphates may be used as bleaching agents in two ways, either oxygen or chlorine being liberated as desired The former is the normal action. To develop chlorine, the cotton may be warmed with a solution of potassium persulphate and sodium chloride. The authors have made rather extensive experiments, but have been unable to bleach cotton without at the same time producing considerable quantities of oxycellulose. This is also the experience of other observers

Percarbonates are prepared by methods similar to those used for persulphates The potassium salt has the formula $K_2C_2O_6$ When heated it decomposes, giving potassium carbonate, carbon dioxide, and oxygen—

$$2K_2C_2O_6=2K_2CO_3+2CO_2+O_2$$

In aqueous solution percarbonates liberate hydrogen peroxide, and also when treated with dilute acids—

$$K_2C_2O_6+2H_2O=2KHCO_3+H_2O_2,$$
$$K_2C_2O_6+H_2SO_4=K_2SO_4+2CO_2+H_2O_2$$

Perphosphates were prepared by Alvarez by treating a cooled solution of sodium phosphate with sodium peroxide and adding alcohol—

$$Na_2HPO_4+Na_2O_2+H_2O=NaPO_4+3NaOH$$

Potassium permanganate, $KMnO_4$ or $K-O-Mn\overset{O}{\underset{O}{\leqslant}}=O$, is a very important oxidising and bleaching agent, which has never received the attention it deserves. It is the potassium salt of permanganic acid, $HMnO_4$, which is formed by the union of manganese heptoxide, Mn_2O_7, with water—

$$Mn_2O_7+H_2O=2HMnO_4.$$

When an oxide of manganese is fused with sodium hydroxide in the presence of an oxidising agent, such as potassium nitrate or chlorate, a green mass containing potassium manganate is obtained—

$$MnO_2+2KOH+O=K_2MnO_4+H_2O$$

When the fused mass is dissolved in a large quantity of water it becomes hydrolysed with the formation of potassium permanganate. Thus

$$3K_2MnO_4+2H_2O=2KMnO_4+4KOH+MnO_2$$

A similar change takes place if the mass be dissolved in water and acidified—

$$3K_2MnO_4+2H_2SO_4=2KMnO_4+2K_2SO_4+MnO_2+2H_2O.$$

The manganese dioxide which is formed is allowed to settle, and the clear

solution is concentrated till it crystallises, when purple crystals of potassium permanganate are obtained These are purified by recrystallisation. Instead of decomposing the potassium manganate by water or acid, a more concentrated solution may be treated with chlorine or ozonised air The reactions in these cases are—

$$2K_2MnO_4+Cl_2=2KCl+2KMnO_4,$$
$$2K_2MnO_4+H_2O+O_3=2KOH+2KMnO_4+O_2$$

Potassium permanganate forms purple crystals with a greenish lustre which contain no water of crystallisation It is somewhat sparingly soluble in cold water, 100 c.c dissolving 4·3 grammes at 10° C It is, however, readily soluble in hot water Its solutions have a deep purplish colour if concentrated and pinkish purple when dilute They have also a peculiar and characteristic taste

When heated, it is decomposed with the evolution of oxygen and formation of potassium manganate and manganese dioxide –

$$2KMnO_4=K_2MnO_4+MnO_2+O_2$$

It is, also, very readily decomposed by concentrated sulphuric acid with evolution of oxygen—

$$4KMnO_4+6H_2SO_4=2K_2SO_4+4MnSO_4+6H_2O+5O_2.$$

When potassium permanganate is heated with concentrated sulphuric acid this reaction is so rapid as to cause an explosion, but it is not decomposed by dilute acid even when boiling *unless some oxidisable body is present.*

Thus, when heated with hydrochloric acid, chlorine is evolved thus

(1) $2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O$
(2) $10HCl+5O \quad =5H_2O+5Cl_2$

Potassium permanganate owes its oxidising action to the fact that manganese heptoxide is a peroxide, which readily gives up a portion of its oxygen, forming manganese dioxide, MnO_2, and sesquioxide, Mn_2O_3, or monoxide, MnO—

$$Mn_2O_7=2MnO_2+3O,$$
$$Mn_2O_7=Mn_2O_3+4O,$$
$$Mn_2O_7=2MnO+5O$$

If cotton be soaked in an aqueous solution of potassium permanganate, it becomes coated with a brown deposit consisting of these mixed oxides The solution, at the same time, becomes alkaline in reaction This process is used in dyeing cotton manganese brown. The alkalinity of the solution is due to the formation of potassium hydroxide—

(1) $Mn_2O_7.K_2O \quad =2MnO_2+K_2O+3O$
(2) $Mn_2O_7.K_2O \quad =Mn_2O_3+K_2O+4O$
(3) $2K_2O+2H_2O=4KOH$

When a considerable excess of sulphuric acid is present these oxides are not deposited, the action taking place somewhat differently Probably permanganic acid is first liberated This then gives up oxygen, becoming changed into manganous oxide This oxide then dissolves in the sulphuric acid, giving soluble manganese sulphate—

(1) $2KMnO_4+H_2SO_4=K_2SO_4+2HMnO_4$
(2) $2HMnO_4 \quad =2MnO+H_2O+5O$
(3) $2MnO+2H_2SO_4=2MnSO_4+2H_2O.$

Or, adding these together—

$$2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O.$$

Thus, two molecules of potassium permanganate contain five atoms of oxygen available for oxidation or bleaching. When this reaction takes place in the presence of an oxidisable substance, the oxygen, being in the nascent condition, has great chemical activity

The following are illustrations of the oxidising action of potassium permanganate, some of which are of importance in the textile industries --

1 Sulphurous acid is oxidised to sulphuric, or sulphites to sulphates--

$$2KMnO_4+5H_2SO_3=K_2SO_4+2MnSO_4+3H_2O+2H_2SO_4$$

This reaction is employed for removing sulphurous acid from woollen goods after stoving

2 Ferrous salts are oxidised to ferric compounds Thus, with ferric sulphate--

$$2KMnO_4+8H_2SO_4+10FeSO_4=K_2SO_4+2MnSO_4+5Fe_2(SO_4)_3+8H_2O.$$

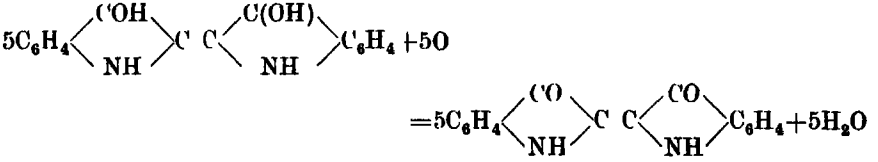
3 Oxalic acid is oxidised to carbon dioxide and water—

$$(1)\ 2KMnO_4+3H_2SO_4=K_2SO_4+2MnSO_4+3H_2O+5O.$$
$$(2)\ 5C_2H_2O_4+5O=10CO_2+5H_2O$$

4 Potassium iodide is oxidised to iodine—

$$10KI+5O=5K_2O+5I_2,$$
$$5K_2O+5H_2SO_4=5K_2SO_4+5H_2O.$$

5 Many *leuco compounds of dyestuffs* are oxidised to the original colouring matter from which they were formed by reduction Thus, indigo white is oxidised to indigo blue—



6 Very many dyestuffs are oxidised into mixtures of simpler colourless and soluble compounds when boiled with potassium permanganate and sulphuric acid

It has been mentioned already that it is possible that traces of ozone are formed when oxygen is evolved from a mixture of potassium permanganate and sulphuric acid.

The action of potassium permanganate on hydrogen peroxide has been described on p. 505

Potassium Permanganate as a Bleaching Agent.—Two molecules of potassium permanganate contain five atoms of available oxygen. This is equivalent to 25·3 per cent The percentage of available oxygen is greater than that of sodium peroxide, and the whole of it may be utilised for bleaching.

When cotton is soaked in an aqueous solution of potassium permanganate it is both bleached and dyed brown at the same time, but the bleaching action only becomes apparent when the oxides of manganese are removed. They cannot be washed away with water, nor are they soluble in a dilute acid But

if the cotton be treated with sulphurous acid, the oxides are reduced to manganous oxide, which is readily soluble in acids—

$$MnO_2+SO_2+H_2O=MnO+H_2SO_4,$$
$$=MnSO_4+H_2O,$$
$$Mn_2O_3+SO_2+H_2O=2MnO+H_2SO_4,$$
$$2MnO+2H_2SO_4=2MnSO_4+2H_2O$$

If some of the brown cotton be put into a bath of sulphurous acid, the oxides of manganese are immediately reduced and dissolved, and it will be seen that the cotton is bleached

But this method could not be used, since potassium hydroxide is produced in the first stage, and oxidising agents in the presence of caustic alkali produce oxycellulose and consequently tendering Hence, the alkali must be removed or neutralised This may be done in two ways, viz —

1 By keeping the bath acid

2 By adding magnesium sulphate to the bath in order to replace potassium hydroxide by magnesium hydroxide

Both methods are used, but the former is generally preferred Sulphuric acid is employed Hydrochloric acid would not do, because, as noted above, it would be oxidised to chlorine

According to the equation given above, two molecules of potassium permanganate require three of sulphuric acid But if only this quantity be used the oxides are still deposited, and must be reduced before they can be removed This means that some of the available oxygen is wasted, and this adds to the expense of the process

When a solution containing about 5 per cent of sulphuric acid is employed, no oxides are deposited on the cotton and the whole of the available oxygen is utilised But there is another and better method of utilising the whole of the available oxygen If the cotton be treated with potassium permanganate and only a little sulphuric acid, so that it becomes coated with the oxides of manganese, and is then put into a bath containing acidified hydrogen peroxide or an acidified solution of sodium peroxide, mutual decomposition takes place with the evolution of the rest of the available oxygen of the permanganate, together with that of the peroxide—

$$MnO_2+H_2O_2=MnO+H_2O+O_2,$$
$$Mn_2O_3+H_2O_2=2MnO+H_2O+O_2$$

If sulphuric acid be present the manganous oxide is dissolved, and at the same time a further bleaching effect is produced

Before describing the methods used, it may be said that there is some prejudice against the use of permanganate, as it is thought to produce tenderness (*i.e.* oxycellulose) This prejudice arose because faulty methods were used If proper precautions are taken there is less danger of producing tenderness than when using bleaching powder One of the authors has made quite extensive comparative experiments, the results of which indicate that the white obtained with potassium permanganate is better and more durable than that given by either bleaching powder or sodium hypochlorite, and is equal to that produced by peroxide The copper number is also lower than that of cotton bleached by any chlorinated bleaching agent

Methods of Bleaching Cotton with Permanganate.—The quantity of potassium permanganate required varies with the nature of the cotton and the

efficiency of the preliminary processes, but as a rule from 0·2 to 0·4 per cent. on the air-dry weight of the goods is sufficient

1 *Neutral Bath Process.*—The permanganate is dissolved in water, and sufficient Epsom salt is added to replace the potassium hydroxide by magnesium hydroxide. From the equations given above it is seen that 316 parts of permanganate require 246 of Epsom salt Hence, for each part of permanganate 0·8 to 1·0 part of crystalline magnesium sulphate should be taken.

The wet goods are soaked in this solution at atmospheric temperature for three or four hours. They are then placed in a cold bath of either sulphurous acid or diluted hydrogen peroxide and finally washed with water. When bleaching with permanganate, the degree of bleaching can be tested by withdrawing a small sample and dipping it in a solution of sulphurous acid Both sulphurous acid or peroxide baths may be used several times.

2 *Acid Bath Method* —The potassium permanganate (from 0·2 to 0·4 per cent.) is dissolved in water and an equal quantity of sulphuric acid is added— $2KMnO_4$ requires $3H_2SO_4$ The goods are soaked in this solution for from three to four hours at atmospheric temperature The quantity of acid used is insufficient, as explained above, to keep the oxides of manganese in solution. The goods are therefore steeped in either dilute sulphurous acid or acidified peroxide solution. If peroxide be used a further bleaching effect is produced. After reducing and dissolving the oxides of manganese, the goods are washed thoroughly with water.

Delebecque (*J.S C I*, 1910, p. 1006) immerses the cotton in a 0 05 per cent solution of sulphuric acid for ten minutes and then in a 3 per cent. solution of potassium permanganate for from three to five minutes. The oxides of manganese are then removed by a bath of hydrogen peroxide Ristenpart (*J. Text Inst*, 1924, A32) recommends the use of a bath containing 1 gramme per litre of permanganate at a temperature of 20° C. for three hours

If a cold solution of sulphuric acid of about 5° Tw strength be used the oxides of manganese are not precipitated Since all the available oxygen is now made use of, less permanganate is required than when only a small quantity of acid is employed. The cotton is steeped for half an hour in the acid, and the permanganate, previously dissolved in water, is then introduced in several portions. After bleaching, the goods are washed with water No treatment with sulphurous acid nor peroxide is necessary This process appears to have been recommended first by Manzoni, who steeped the cotton in sulphuric acid of 7½° Tw density and used about 0 5 parts of permanganate for each 100 of cotton

The acid baths are better than the neutral baths Kind (*J S.C I*, 1920, 16A) states that the oxygen is rendered less active by the presence of magnesium hydroxide Ristenpart (*loc cit*) concluded, also, that acid baths give the best whites, but if a product with the highest tensile strength is required neutral baths are better, though at the sacrifice of some brilliancy of colour. The experience of the authors is that if the acid bath is used carefully there is no diminution of tensile strength.

Potassium bichromate (or dichromate), $K_2Cr_2O_7$, although not used as a bleaching agent, may be mentioned, since it is of considerable importance in other textile operations. It is very similar in its properties to potassium permanganate, containing three atoms of loosely combined oxygen.

It is made by fusing chrome ironstone with potassium hydroxide, or carbonate, in the presence of air. Potassium chromate, iron oxide, and carbon dioxide are formed—

$$4Cr_2O_3.FeO+8K_2CO_3+7O_2=8K_2CrO_4+8CO_2+2Fe_2O_3.$$

The soluble chromate is separated from the fused mass by extraction with water The solution is then treated with sulphuric acid, which converts the potassium chromate into bichromate—

$$2K_2CrO_4+H_2SO_4=K_2Cr_2O_7+K_2SO_4+H_2O$$

Potassium bichromate is only sparingly soluble in water, and can be obtained by concentrating and crystallising the solution

Potassium bichromate is a red crystalline substance At 10° C 100 parts of water dissolve 8 parts of the salt, and at 100° C 96 parts It is the salt of dichromic acid $H_2Cr_2O_7$, which is itself derived from chromic acid, thus

$$2H_2CrO_4-H_2O+H_2Cr_2O_7$$

Chromic acid is formed by the combination of chromium trioxide with water—

$$CrO_3+H_2O=H_2CrO_4$$

Hence, dichromic acid is also a derivative of chromium trioxide Chromium trioxide (or chromic anhydride) is obtained when a cold concentrated solution of potassium bichromate is treated with sulphuric acid

$$K_2Cr_2O_7+2H_2SO_4-2CrO_3+2KHSO_4+H_2O$$

The chromic anhydride crystallises from the solution in dark red crystals When a solution of potassium bichromate is treated with an alkali it is converted into potassium chromate

$$K_2Cr_2O_7+2KOH=2K_2CrO_4+H_2O$$

Potassium bichromate is a very powerful oxidising agent, but it acts only in presence of an acid This is because chromic acid is first formed which is unstable, breaking down into chromic hydroxide and oxygen—

$$(1)\ K_2Cr_2O_7+H_2SO_4+H_2O=K_2SO_4+2H_2CrO_4$$
$$(2)\ 2H_2CrO_4+H_2O=2Cr(OH)_3+3O$$

It is evident from these equations that one molecule of potassium bichromate contains three atoms of oxygen available for oxidising purposes In the presence of sulphuric acid the chromic hydroxide produced in equation (2) is dissolved to form chromic sulphate—

$$2Cr(OH)_3+3H_2SO_4=Cr_2(SO_4)_3+3H_2O$$

A mixture of potassium bichromate and sulphuric acid is used for stripping dyestuffs from textile fabrics When potassium bichromate is strongly heated, oxygen is liberated in accordance with the equation

$$4K_2Cr_2O_7=4K_2CrO_4+2Cr_2O_3+3O_2$$

If potassium bichromate be heated with hydrochloric acid the oxygen liberated oxidises the excess of acid to chlorine—

$$K_2Cr_2O_7+14HCl=2KCl+2CrCl_3+7H_2O+3Cl_2$$

This forms a convenient method for preparing small quantities of chlorine

Other examples of the oxidising action of potassium bichromate are—

1 It oxidises ferrous sulphate to ferric sulphate—

$$6FeSO_4+K_2Cr_2O_7+7H_2SO_4=3Fe_2(SO_4)_3+Cr_2(SO_4)_3+H_2SO_4+7H_2O$$

2 Sulphur dioxide, or its compounds, are oxidised to sulphuric acid or sulphates—

$$K_2Cr_2O_7+4H_2SO_4=K_2SO_4+Cr_2(SO_4)_3+4H_2O+3O,$$
$$3H_2SO_3+3O=3H_2SO_4$$

3 Iodine is liberated from potassium iodide in the same way as chlorine is from hydrochloric acid—

$$K_2Cr_2O_7+6KI+14HCl=8KCl+2CrCl_3+7H_2O+3I_2$$

The Air as a Bleaching Agent.—Atmospheric oxygen is the oldest known bleaching agent It is still used for household goods and linen It owes its action partly to traces of ozone and hydrogen peroxide Country air contains 1 part of ozone by volume in 700,000 More is present in spring than in summer, and more in summer than in winter It is more abundant on rainy than on fine days, and its presence is favoured by west or south west winds Air, *per se*, is of little use as a bleaching agent in the absence of diffuse sunlight Its bleaching action is only developed under the influence of actinic rays In the neighbourhood of towns, the atmosphere is contaminated with suspended matter and putrefactive organisms, and the exposure of goods out of doors results, commonly, in their becoming spotted with soot and other impurities It is only in country districts that exposure to air is practicable But the process of bleaching by air is very slow Cotton bleaching is essentially a 'quick' trade Goods must be bleached and delivered, often, within a day of receipt This alone makes the use of atmospheric oxygen impracticable under ordinary conditions But interesting attempts have been made to accelerate the process Muller (*J S C I*, 1910, p 1200) patented the following process The goods are treated at a high temperature, and under pressure, with an aqueous solution of sodium or calcium hydroxide, through which a current of air is forced The bleaching is accelerated by the addition of a small quantity of a salt, such as manganese carbonate, which acts as an oxygen carrier In a later addition (*J S C I*, 1911, p 534) further details are given Sixty kg of cotton and 1000 litres of a 1 per cent solution of sodium carbonate, containing 20 grammes of manganese sulphate, are put into an autoclave, care being taken that the cotton is completely covered with the lye The kier is then heated for two hours under a pressure of 2 atmospheres, air being excluded A current of air, at a pressure of 1 to 1 5 atmospheres greater than the steam pressure, is next directed on to the surface of the lye until the bleaching operation is complete The lye is then run off, the cotton washed and treated for a minute with a 0 5 per cent solution of sodium bisulphate, to remove the precipitated oxides of manganese It is then washed again, and finally dried If this process were practicable it would be very valuable, because the lye boiling and bleaching are carried out practically simultaneously The authors have made laboratory tests of the method They found that while there is no doubt about the bleaching, the bleached cotton was always tendered, owing to the formation of oxycellulose The same criticism applies also to a later process by Anders (*J S C I*, 1918 121A), who wets out the cotton with hot milk of lime and then bleaches it in a bath of the same liquor, containing also an oxygen carrier, by means of a current of air

Some experiments described by Thorne (*J S C I*, 1914, p 729) indicate that atmospheric oxygen might be used in connection with bleaching powder solutions with advantage He found that in the bleaching of paper pulp by means of bleaching powder, the amount of chlorine required could be decreased by from 30 to 50 per cent by the introduction of oxygen in a state

of very fine division. In the absence of bleaching powder oxygen had no bleaching effect

Ozone, O_3, is produced by the action of a silent electric discharge upon air or oxygen Atmospheric ozone is formed in this way, and also by the action of the ultra-violet on atmospheric oxygen. Traces of ozone are produced, also, during the slow oxidation of many substances If a stick of clean phosphorus be placed in a jar of moist air, the presence of ozone can soon be detected by its peculiar smell and power of liberating iodine from potassium iodide This reaction may, perhaps, be represented by the equation

$$4P+2O_2=P_4O+O_3.$$

Traces of ozone are produced, together with oxygen, by many chemical reactions For example, a mixture of potassium permanganate and sulphuric acid owes its peculiar smell partly to the liberation of traces of ozone

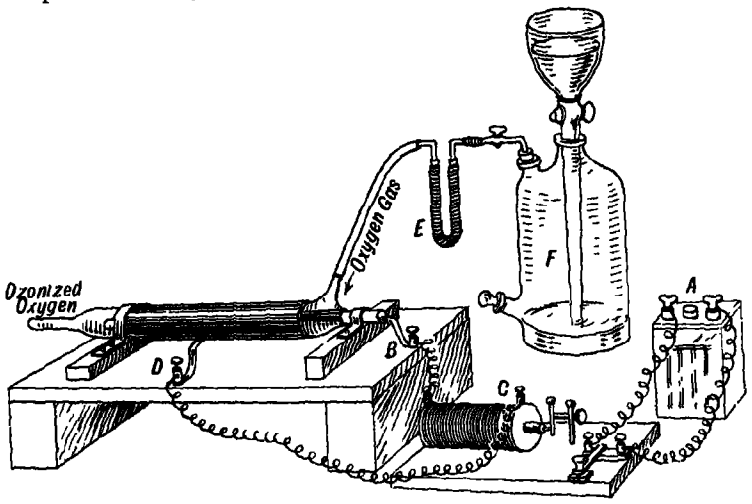


Fig 176.—Siemens Ozoniser

Ozone cannot be prepared alone, but only mixed with air or oxygen Ozonised air is made by subjecting air to a silent electric discharge The apparatus of Siemens is illustrated in fig 176. It consists of two concentric tubes. The inner tube is coated on its inner surface with tinfoil, which is in metallic contact with the terminal B, and the outer tube is coated on its outer surface with tinfoil which is in metallic contact with the terminal D The two terminals are connected to an inductor coil. A slow stream of oxygen is passed from the gasholder F, first through a drying tube, E, containing calcium chloride, and then through the annular space between the concentric tubes, where it is exposed to the action of the silent electric discharge produced by the battery A and induction coil C The gas issuing from the ozoniser contains from 3 to 8 per cent of ozone. It is important that the apparatus should contain no exposed rubber points or corks, since both of these substances decompose ozone.

The reaction $3O_2 \rightleftharpoons 2O_3$ is reversible, and this explains why only a limited quantity of ozone can be produced when air is passed through the ozoniser.

On the commercial scale ozonised air may be obtained by the apparatus shown in fig. 177, which is made by the Ozonair Co., Ltd.

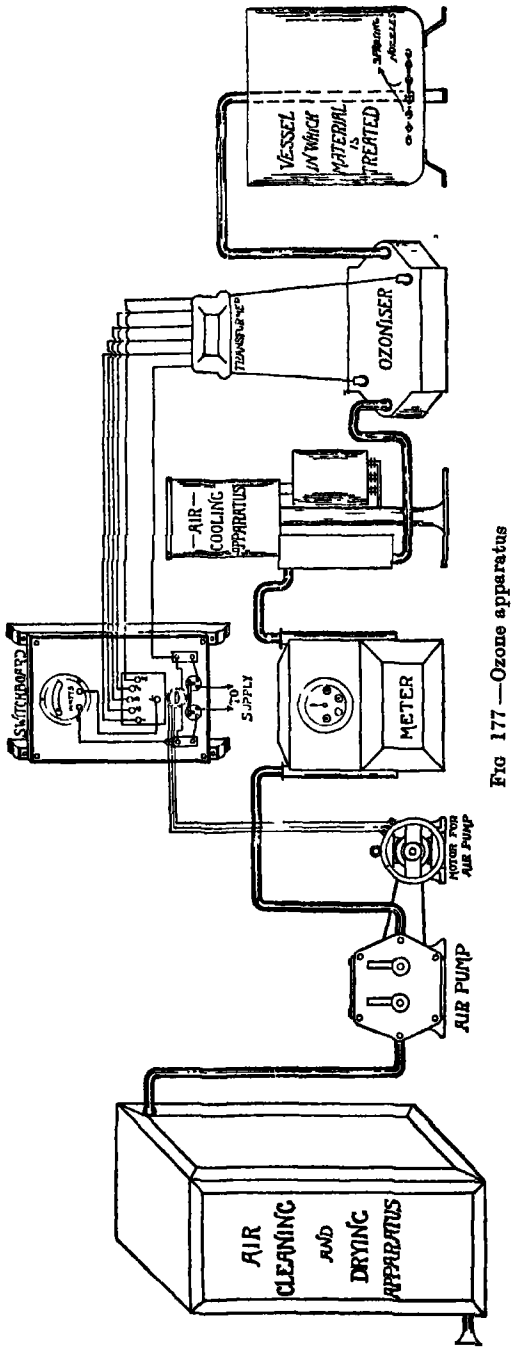


FIG 177.—Ozone apparatus

Ozone may be prepared also by allowing air to act upon mixtures of organic substances, as in the method of Georgevics, in which a mixture of resin, turpentine, and hydrogen peroxide is used The ozone dissolves in the turpentine, from which it can be extracted subsequently by washing with water.

Properties of Ozone.—Ozone has a strong and characteristic smell. It is soluble in water, one hundred volumes of water dissolving one volume of ozone at ordinary temperatures It dissolves, also, in turpentine and certain other inorganic liquids Ozone can be separated from ozonised oxygen by passing the latter through a tube immersed in boiling liquid oxygen In this way a solution of ozone in liquid oxygen is obtained If most of the oxygen be then allowed to evaporate, a deep blue liquid, rich in ozone, is obtained When ozone is kept at ordinary atmospheric temperatures it changes gradually into oxygen If ozonised air be heated to a temperature of 300° C , the ozone it contains is completely decomposed Ozone is an extremely powerful oxidising agent Thus, it oxidises silver to silver oxide, a change which cannot be brought about by means of oxygen Mercury is also changed into mercuric oxide when exposed to the action of ozonised air—

$$Ag_2+O_3=Ag_2O+O_2,$$
$$Hg+O_3=HgO+O_2$$

Other examples of the oxidising action of ozone are—

1 It liberates iodine from potassium iodide—

$$2KI+O_3+H_2O=2KOH+I_2+O_2$$

This reaction is used as a means of detecting ozone in air If a piece of filter-paper, moistened with a solution of potassium iodide and starch, be exposed to air containing ozone, the blue colour of iodide of starch is at once produced. If a known volume of ozonised air be passed through a solution of potassium iodide and the liberated iodine titrated with decinormal sodium thiosulphate, the ozone present may be estimated

2. Lead sulphide is oxidised by ozone to lead sulphate—

$$PbS+4O_3=PbSO_4+4O_2.$$

3 Many colouring matters, such as a moistened litmus paper, are bleached when exposed to the action of ozonised air

4 Many micro-organisms are destroyed by ozone Ozonised air is, on this account, used in the ventilation of the air in large buildings or underground railways

When ozone is brought into contact with metallic peroxides (*e g* manganese peroxide, MnO_2) or finely divided platinum, it is changed into ordinary oxygen, the metal or oxide acting as a catalytic agent

The oxidising action of ozone depends upon the fact that the molecule splits up readily in accordance with the equation

$$O_3=O_2+O.$$

A molecule and an atom of oxygen are produced, and the latter being in the nascent state exhibits great chemical activity. When ozone is heated alone, the two liberated atoms combine to form a molecule, since an atom cannot exist in the free state—

$$O_3+O_3=O_2+O+O_2+O=3O_2$$

For similar reasons ozone acts, also, as a reducing agent when brought into

contact with bodies containing another atom of loosely combined oxygen Hydrogen peroxide is an example—

$$H_2O_2+O_3=H_2O+2O_2$$

Or in the case of sodium peroxide dissolved in water—

$$Na_2O_2+H_2O+O_3=2NaOH+2O_2$$

The Constitution of Ozone.— Ozone is regarded as a condensed form of oxygen, three volumes of the latter giving two volumes of ozone Its constitution is not yet fully understood It has been represented by the following formulæ —

(1)  , (2) O O O O, (3) 

The fact that three volumes of oxygen form two of ozone may be proved by the following experiment –

A quantity of oxygen is confined in a graduated barometer tube over sulphuric acid, and subjected to the action of an electric spark At first an expansion is observed, but when the gas has cooled again, it will be seen to have diminished in volume This contraction is measured, and then a few drops of turpentine are introduced into the tube by means of a small pipette Turpentine dissolves ozone, but not oxygen A further contraction will be observed, corresponding to the amount of ozone present before the introduction of the turpentine From these measurements the relation of the volume of ozone to the volume of oxygen, from which it has been produced, can be inferred The following is an illustration of the method —

Volume of original gas	—100 c c
Volume of oxygen+ozone	= 99 c c
Volume of oxygen after the removal of ozone	– 97 c c
Volume of oxygen converted to ozone	—100 97 3 c c
Volume of ozone	— 99 97 2 c c

This is expressed by the formula O_3

Further proof is found that the rate of diffusion of ozone corresponds with the formula O_3

Ozone as a Bleaching Agent.—Ozonised air is used as a bleaching agent for oils, and is said to replace successfully the " grassing " operation in the bleaching of linen, particularly if the material be treated, first, with some liquid, such as turpentine, which absorbs ozone

Reference has been made to the saving of chlorine effected in the bleaching of cellulose by passing a current of air through the liquor Ozonised air is said to be still more effective Ozonair Ltd state that with concentrations of 0 5 grammes or less of ozone per cubic metre of air cotton can be bleached successfully without causing the production of oxycellulose The action of ozone on cotton has been described on p 120

Chloramine T (or activin) is the sodium salt of para-toluene sulpho chlor amide and has the formula

$$CH_3\,C_6H_4\,SO_2\,N(Cl)Na+3H_2O$$

It is made by treating an aqueous suspension of para toluene sulphonamide with bleaching powder and double decomposition of the calcium salt with sodium chloride The sodium salt which separates is purified by recrystallisation from hot water

Chloramine is a colourless crystalline body which is sparingly soluble in cold water. Its aqueous solution is comparatively stable, and can be boiled without decomposition if oxidisable substances are absent But in the presence of the latter decomposition takes place, with formation of para-toluene-sulphonamide and oxygen—

$$CH_3\,C_6H_4\,SO_2\,N\begin{matrix}Cl\\ \diagup\\ \diagdown\\ Na\end{matrix} + H_2O = CH_3\,C_6H_4\,SO_2NH_2 + NaCl + O$$

A solution of chloramine T has very powerful antiseptic properties even at dilutions of 1 in 100,000. The calcium salt is used as a weed killer. It may be used also as a bleaching agent, and the para-toluene-sulphonamide which is formed has no action on cotton A solution containing 1 part in 5000 of water is suitable At ordinary temperatures its action is slow, but the rate of bleaching is accelerated by heating It may be used also for the preparation of solutions of soluble starch, about 1 per cent being necessary for this purpose

CHAPTER XXVII.

PROCESSES.

Introduction.

HAVING reviewed the apparatus employed in manipulating the cloth in the different processes, and studied the nature of the chemicals used and the reactions which take place in rendering the impurities soluble, the systematic arrangement, or sequence, of the component parts of the process may now be considered under the designation "Methods of Bleaching," or "Methods." Both sequence and combination depend upon the particular requirements with regard to the goods to be treated In dealing with cloth the method of bleaching may be expressed, generally, by stating the "runnings" employed, and defined more exactly by specifying the duration of the treatments thus referred to, the strength of the solutions used, and the temperature or pressure at which the reaction is carried out

The severity of the processes depends upon the "degree of bleaching" required. There are certain recognised standards which may be referred to. These are--

1 *The Full Bleach*—This term denotes the highest standard of quality. The cloth must be freed completely from its impurities and have a perfect and durable white colour It is required for high-class goods which are to be finished without the use of "assistants" or "filling" agents.

2 *The Half Bleach*—For this a somewhat lower standard of freedom from impurities and a less pure white are necessary This type of bleach is employed for goods which are to be weighted or assisted in finishing.

3 *Bleach for Dyeing and Printing*—The nature of this depends upon the dyestuffs to be used For heavy shades and dark colours, permeability and freedom from impurities which would affect the colour are of more importance than a perfect white Where, however, light shades or bright colours are to be used, the bleaching must be more thorough

4. *Bleach for Coloured Goods.*—In bleaching coloured goods, the chief object is to bleach the undyed parts of the fabric without at the same time altering the colour.

Both general and detailed examples of different methods are given below, and certain additional processes for goods other than cloth are dealt with subsequently. The methods adopted vary with the nature of the goods and the result required, and to a certain extent with the locality and idiosyncrasy of the bleacher. Hence those given in this chapter must be regarded as examples only, and not as standard methods incapable of variation. The good bleacher, in fact, should always be trying by judicious variation of his processes, thought out upon some

rational plan, to improve the quality or efficiency of his work The reactions in themselves are, as we have seen, simple in nature, consisting in the removal by saponification, and similar means, of the natural fats, pectins, proteins, and colouring matters of the cotton, together with dirt and other matter introduced during manufacture

The difficulty arises in rendering these bodies completely soluble without at the same time *damaging* the goods themselves In practice it is found, in many cases, very difficult to complete each operation before proceeding to the next. Thus the series is frequently repeated in part or altogether, with the idea of attacking and removing successive layers of impurities. The simple series of operations, viz steeping, lye boiling, bleaching, and souring, is in many cases sufficient, and when every process is thoroughly and scientifically carried out would still be sufficient in many others where a more complicated procedure is adopted There is no doubt that a good deal of the repetition found to be necessary is not so much due to the obstinacy with which the cotton retains its impurities *as to the absence of the conditions most favourable to the completeness of the reactions* In the following methods, the necessity for washing is taken for granted There is nothing more important than thorough washing between the processes The reactions only render the impurities soluble in water, but much of this is required to remove them, and incomplete washing at any point only causes the impurities, which should be absent, to be carried on to the next process, where they are, as a rule, again fixed on the goods, thus making the repetition of the former process necessary This is, in fact, not infrequently the cause of the repetition of processes The factors regulating the method which must be adopted include—

1 The nature of the goods to be treated, the subsequent treatment for which they are designed, and the degree of bleaching required
2 The character of the water used.
3 The efficiency of washing and other appliances.
4 The type of kier employed.
5 The personal equation of the bleacher

The character of the goods which have to be treated is very varied, ranging from heavy moleskin to butter-cloth and finest lace, and including (in order of difficulty with regard to bleaching), shirtings, piqués, drills, sateens, sheetings, medium shirtings, jaconets, nainsooks, light shirtings, lace and curtains, muslin, lawns, net and mulls, etc Coloured goods are dealt with separately. Each of these classes of goods may be treated by different methods to produce the same result, those described must only be regarded as examples of those in actual use They are all, of course, capable of improvement and shortening, depending upon the factors cited above

The methods given are summarised in the tables on pp 531 and 534

The first table refers to methods in which the lime boil is used, and presents several arrangements which are tabulated in descending order of severity of treatment They may be regarded as alternative schemes. The first four are methods employed in producing the "madder bleach," used in treating the heaviest goods, which are difficult to bottom

The second table gives a similar set of illustrations of methods in which the lime boil is replaced by caustic soda In the subsequent examples the strength of the chemics are given in degrees of chlorine contents The relation between specific gravity (Twaddell) and chlorine content is shown in the table given on p. 459.

1	HP Lime boil	Lime sour	1st Bowk HP	1st Ch and Sr	2nd Bowk HP	2nd Ch. and Sr		
2	LP Lime boil	Lime sour	1st Bowk LP	1st Ch and Sr	2nd Bowk LP	2nd Ch and Sr	3rd Bowk LP	3rd Ch. and Sr.
3	LP Lime boil	Lime sour	1st Bowk LP	2nd Bowk LP	1st Ch and Sr	3rd Bowk LP	2nd Ch and Sr	
4	LP Lime boil	1st Bowk LP	1st Ch and Sr	2nd Bowk LP	2nd Ch and Sr	3rd Bowk LP	3rd Ch and Sr	
5	LP Lime boil	Lime sour	1st Bowk LP	2nd Bowk LP	3rd Bowk LP	Ch and Sr		
6	LP Lime boil	Lime sour	1st Bowk LP	1st Ch and Sr	2nd Bowk LP	2nd Ch and Sr		
7	LP Lime boil	1st Bowk LP	1st Ch and Sr	2nd Bowk LP	2nd Ch. and Sr			
8	LP Lime boil	1st Ch and Sr	1st Bowk LP	2nd Ch and Sr				
9	LP Lime boil	Lime sour	1st Bowk	1st Ch and Sr				

HP = High pressure.
LP = Low pressure.
Ch = Chemic.
Sr = Sour

Example Method 1 —

"Madder bleach" for heavy shirtings, or for printers for white ground which require steaming Singe, steep and wash

Then saturate with lime with machine, using 1¼ to 1½ cwt of lime per ton of cloth, and pass into the kier

Boil for eight hours at 20 lbs pressure, then wash off in the kier

After thorough washing, sour with hydrochloric acid of 2° Tw, wash through two machines in tandem into a kier containing 35 to 40 lbs of soda ash and 15 to 20 lbs of rosin per ton of cloth, and boil for eight hours at 10 to 15 lbs pressure Wash off in the kier and then again through the washing machine into the chemic tank Circulate the chemic [1] (1°) for two and a half hours Then drain and pass through washing machine into the souring tank Circulate in the sour (½° Tw HCl) for two and a half hours Then pass again through the washing machine into the second lye boil of half the strength of the first and boil for eight hours at 5 lbs pressure Wash off in the kier and then pass through the washing machine into the chemic tank and circulate for two and a half hours at 2 5° Then wash again, and sour with sulphuric acid of 1° Tw for two and a half hours Then wash twice and squeeze

The difference between Methods 1 and 2 is in the employment of high- or low pressure kiers The effect of the high pressure is to shorten the boil and reduce the number of operations necessary

In Method 2 the low-pressure boil must continue for ten hours, using the same quantities of chemicals

[1] *i e* 1° signifies 1 gramme of available chlorine per litre This term should not be confounded with the "chlorometric degree" referred to on p 457

This form of process is employed when the presence of headings in the cloth precludes the use of the closed kier. Method 1 is not extensively adopted, as closed kiers affording safe and efficient circulation are not yet in very general use.

In Method 3 occurs the precautionary measure of postponing the first chemic to a late stage, while the reverse is the feature of Method 4. The main idea in this case is to utilise the uncombined lime from the lime boil to enhance the causticity of the first bowk, while relying also on the presence of the lime to prevent mercerisation The saving of runnings and the avoidance of risk of excess of acid from the eliminated lime sour is also claimed as a benefit. But the process seems liable to produce lime stains, and this should outweigh any possible gain of whiteness by the early introduction of the first chemic.

Method 7 is an abbreviation of the same method for lower goods. The characteristic feature of Method 3 is extended in Method 5 by the bleacher, who is working for a good bottom and with minor regard for brilliance of white

The following is an example of Method 6 It relates to a 50 cwt lot of nainsooks requiring a hard finish.

1. Steep, wash, and impregnate with lime, and boil for ten hours in L P. kier ; wash out in the kier, and then

2 Wash and sour, through machines, using hydrochloric acid of 2° Tw.

3 Wash into first lye boil, using 70 lbs soda ash, and boil six hours

4 Wash into chemic (1·5°) and circulate for half an hour, and then into sour (vitriol at ½° Tw)

5 Wash into second lye boil, using 18 lbs soda ash, 30 lbs rosin ; boil three and a half hours.

6 Wash into chemic (2°), circulate for half an hour, and then into sour (vitriol at 1½° Tw), circulate for half an hour and wash twice

A point of interest in the above is the introduction of rosin in the second lye boil, the object in this case being to assist in the production of a harsh finish, so that it performs the function of a finishing agent as much as that of a detergent, the cloth having been well scoured before the rosin is applied If used in its more usual capacity and solely as a detergent, it would have been applied in the first lye boil and excluded from the second one, the object of which would then have been to remove traces of insoluble rosin soaps (rosin stains)

Method 6 is frequently abbreviated to the form indicated in Method 8, in which case, if working for a hard finish, the first lye boil would require 90 lbs soda ash and 30 lbs rosin, and the boil would in any case be extended to seven hours' duration and the final chemic increased to 3°.

For a softer finish less rosin would be employed But the omission of a second lye or soap boil increases the risk of rosin stains, and the use of the second boil in any special case is a matter of judgment as to the completeness of the first lye boil

The first bowk in Method 6 is sometimes preceded by a short and weak bowk merely to neutralise any excess of acid brought over from the lime sour This is quite rational, but a double wash out of the sour is equally effective

The following is an example of Method 6 as applied to wide sheetings —

1 Pile in the kier, laying the pieces out separately and evenly
2. Boil for fourteen hours in lime, and wash out the kier with water.
3. Empty the kier and lift the pieces separately into wagons
4. Wash in dash wheel.

5. Remove to cistern and sour with hydrochloric acid of 2° Tw., circulating for three hours.
6. Wash in dash wheel.
7. Boil for ten hours in soda ash
8. Wash in dash wheel
9. Remove to chemic tank and leave overnight with excess of chemic at 2·75°.
10 Wash in dash wheel.
11 Sour with sulphuric acid at 1° Tw , as before
12 Wash in dash wheel.
13 Remove to kier and boil with soda ash for six hours
14 Wash and chemic at 1·5°, as before
15 Wash and sour, as before.
16 Wash and dry

The same treatment applies to towels and white quilts
Method 8 may be applied to the same goods as follows —

1 Lime (medium strength) for ten hours, boiling and washing as above
2 Wash into chemic (6°) Circulate for half an hour
3 Drain and wash
4 Sour with sulphuric acid (2° Tw) Circulate for half an hour, flood for ten minutes, and drain
5 Wash and remove to kier
6 Boil for nine hours with soda and rosin, as above.
7 Wash
8. Remove to chemic, 2·75° Tw Circulate for half an hour, and drain
9 Wash twice

This method is known as the stew-chemic
The following is an interesting method employed for medium shirtings, but may be advantageously replaced by Method 6 —

1 Steep.
2 Lime into kier, adding milk of lime while plaiting
3 Boil at low pressure for twelve hours, then drain off and fill up with warm water and continue boiling for one hour
4 Wash into chemic (2°) Circulate for half an hour, and drain
5 Wash into hydrochloric acid (2° Tw)
6. Wash and boil with soda ash (2 per cent of weight of cloth) and soap (0 25 per cent).
7. Wash into chemic (2·75°) Circulate for half an hour, and drain
8 Wash into sulphuric acid (1° Tw) Circulate for half an hour, drain, and wash twice

An example in contrast with the earlier methods is that applied to butter-cloths —

1. Steep overnight in hot water.
2. Wash into chemic (3°). Circulate for half an hour, and drain
3 Wash twice

Method 9 is the shortest form of the normal type and is used for very light goods, such as mulls and tanjibs. The double bowk and chemic is always preferred, since it removes any deposited rosin due to incomplete action of the first bowk, and generally " tops " the bleach.

In the abbreviated methods, in which the conditions as to over-bleaching are less regarded, the chemic is frequently used at a higher concentration

It will be seen from the above examples that the abbreviations most commonly introduced in practice relate to the suppression of steeping and the sour after the lime boil The omission of the former is generally due to the slight inconvenience entailed and the extra space required, and to the view that the same effect is more simply obtained by an inconsiderable increase in the cost of boiling The omission of lime sour, and especially its substitution by chemicking, is more irrational, and the resulting bleach or finish cannot be as satisfactory as if the normal methods be adopted The most economical and satisfactory working may be obtained by the adoption of a process based on one or other of the Methods 1, 6, or 9, according to the requirements of the case, and the latter two methods may also be rendered more economical and rapid by the employment of high-pressure kiers

In the following table, methods are indicated in which the lime boil is omitted, caustic soda being used in its place —

1	Hot Sour	HP Caustic boil	Ch and Si			
2	HP Caustic boil	HP Ash boil	1st Ch and Si	LP Ash boil	2nd Ch and Si	
3	HP Caustic boil	1st Ch and Si	LP Ash boil	2nd Ch. and Si	Soap scald	3rd Ch and Si
4	HP Caustic boil	(Salts) Sr.	LP Ash boil	1st Ch. and Sr	Soap scald	2nd Ch and Si.
5	HP Caustic boil	1st Ch and Si	LP Ash boil	2nd Ch and Si		
5a	LP Caustic boil	1st Ch and Si	LP Ash boil	2nd Ch and Si.		
6	HP Caustic boil	HP Caustic boil	Sour			
7	HP Caustic boil	LP Ash	Ch and Sr			
8	HP Caustic boil	Ch and Sr.				
9	LP Impregnating	Pile	Ch and Sr			

Method 1 applies to the Thies Herzig system and has been already described

Of the various groupings given, Method 2 is probably the most effectual for obtaining a full bleach with minimum risk of leaving fatty and pectinous bodies on the one hand, and avoiding over-bleaching on the other

Method 3 is the one most usually adopted The last two treatments are only brief, as it is not advisable to push the process beyond the second chemic.

Example of Method 2 applied to heavy shirtings—

1 Steep, wash, and impregnate with lye

2 Boil in high pressure kier for seven hours at 40 lbs pressure with 3 per cent Na_2O on the weight of the goods

3 Run off liquor, and wash in the kier and then through machines

4. Boil again for seven hours in soda lye (80 per cent NaOH and 20 per

cent carbonate), using 1½ per cent Na_2O on the weight of goods and ¾ per cent. rosin

5 Wash in kier and machine
6 Chemic (2 5°) Circulate for two and a half hours, and drain
7 Wash through machines into sulphuric acid (1° Tw)
8 Wash into lye boil, using 1½ per cent sodium carbonate (and 0 5 per cent rosin size, or soap, according to finish) Boil at low pressure for four hours
9 Wash through machines
10 Chemic (2°) Circulate for two hours, and drain
11 Wash into sulphuric acid 1° Tw , as above
12 Wash and squeeze

Method 4 is designed to emphasise the preparatory scouring effect and to defer the first chemic to a later stage The souring process between the boils must be followed by a very complete washing or it will do more harm than good, and render the soda ash boil under pressure dangerous, owing to the liberation of carbon dioxide

Example of Method 5 for two ton lot of heavy shirtings

1 Steep, and wash into kier
2 Boil for eight hours at 15 to 20 lbs pressure with lye containing 20 lbs caustic soda powder, 80 lbs rosin and 1 lb cresol
3 Wash into chemic (2 75) Circulate for two hours
4 Wash into sour (2 Tw) Circulate for two hours
5 Wash into kier and boil for seven hours with 120 lbs soda ash
6 Wash into chemic (2 75) Circulate for two hours
7 Wash into acid as above
8 Wash and squeeze

Method 5*a* is characterised by the omission of pressure from the caustic boil This is sometimes done as a precautionary measure in dealing with delicate goods which must be kept under supervision, or to facilitate the early removal of special goods

It is, however, attended with considerable liability to tendering, owing to presence of air and it is most important to keep the cloth well submerged beneath the liquor if this danger is to be averted Whenever possible, it is preferable to effect the caustic boil with at least sufficient pressure to exclude the air

Example of Method 5 applied to a two ton lot of medium shirtings—

1 Wash, impregnate and boil at 20 lbs pressure for eight hours with 70 lbs caustic soda, 30 lbs rosin, and 1 lb cresol
2 Wash into chemic (2 75°) and circulate for two hours
3 Drain and wash into sulphuric acid (1° Tw)
4 Wash into kier and boil with 120 lbs soda ash for seven hours
5 Wash into chemic (2 75°) and circulate as above
6 Drain and wash into sour, as before
7 Wash and squeeze

Example of Method 5a applied to a two-ton lot of curtains and muslins—

1 Wash into kier and boil at low pressure for seven hours with 60 lbs caustic soda (and 30 lbs rosin size)
2 Wash thoroughly into chemic (2°) and circulate for half an hour

3. Drain and wash into sulphuric acid (1° Tw).
4. Wash into kier and boil for six hours at low pressure with 10 lbs. caustic soda, 60 lbs sodium carbonate, and 30 lbs soap.
5 Wash out of kier into chemic, and chemic and sour as before.

Method 6 is used in the turkey-red bleach

Example of Method 7 applied to light printers—

1 Steep, and wash into kier
2. Boil for eight hours at 30 lbs pressure, using 40 lbs caustic soda per ton
3 Wash off in the kier for two and a half hours
4 Fill up with soda-ash lye (20 lbs. per ton) and boil again
5 Wash through No 1 machine and chemic through No 2 (with chemic of 6°) into chemic tank and circulate for two and a half hours
6 Drain and wash into hydrochloric acid at 2½° Tw.
7 Wash and squeeze.

Method 7 is a rapid one, the cloth not being removed between the boils, and either this or Method 8 is applicable to the open-bleach systems described, in which the mechanical arrangements are conducive to perfect circulation and consequent reduction of the subsequent operations Method 9 refers to the Edmeston-Bentz system previously described

Example of Method 8 employed in bleaching low nettings—

Wash into kier, and boil for eight hours with 2½ per cent caustic soda, wash through first washing machine, chemic in second machine at 4°, and pile on to stillage Drain and wash in first machine, sour in third machine, and wash twice

The bleaching of lace goods, or those which are too delicate to handle in the rope form, and which, on account of the graphite (used to lubricate the lace-machine bobbins during manufacture), are very dirty, demands special treatment. Also the requirements of the trade are such that very rapid delivery is frequently demanded.

An important feature of the process lies in the manipulation of the lace in the form of bundles, the lace being laid out and folded by hand to conveniently reduce the length of the bundles, which are then tied up by cords and dropped into the boiling kier The disposition of the bundles in the kier is somewhat loose, and is distinct from the method of plaiting previously described. The light and spongy nature of the bundles, however, assists in the effectual circulation of the lye, and the chief precaution is to keep the goods below the liquor.

The boiling liquor containing 2½ to 3 per cent of caustic soda (as compared with the weight of the cloth) must be brought to the boil quickly, and a supply of hot water be kept ready to expedite the making of the lye and the immersion of the fabric in the kier

The boil is in special cases limited to two hours, but a three-hours' boil is more usual.

It is customary to have special smaller kiers to deal with urgent orders and to load these first The subsequent processes are mainly effected in the dollying machine, chemicking and souring tanks, and the hydro-extractor (or " centrifugal ")

Following the boil, the bundles are removed from the kier, " specials " being

sometimes extracted while the rest remain, and taken in hand wagons to the dollies They are there treated with a spray of hot water to rinse out the lye. This is repeated three times during five minutes with half the beaters in action, the second and third application of water being cold. The bundles are then removed to the centrifugal for the extraction of the washing water in preparation for the " grey " bleach. This is effected either by steeping in a cistern or by the cage method already described

The strength of the bleach employed depends entirely upon the time allowed, and is even used at a temperature of 80° to 90° F. to expedite its action. Some bleachers employ a strength of 14 5° for a short time, but any strength above 5·5° is attended with some risk This first chemic occupies one hour, but if warmed at 3°, twenty to thirty minutes is sufficient

The liquor is then allowed to drain away, and the lace removed for cleaning with six " rounds " in cold water in the dollies Then hot water is turned on to cover the goods, and dilute sours added gradually to bring the whole to about ½° Tw

The goods are treated in the dolly with this solution for about one minute, and the sours run off Cold water is now sprayed on to wash out the sours, and then hot water applied and a charge of soap-suds added to make a good lather, and this is worked into the goods for ten minutes

Then the suds are washed out with cold water After expressing the water by running the dolly for several rounds while the cloth is draining, the contents are removed to the white bleach, where they remain for half an hour, or according to colour, and bleached with chemic of 2·75° strength. After draining they are again returned to the dolly to clean with six rounds in cold water The valves are then dropped and the tub flooded for souring, as before, sulphuric acid being added to bring the strength of the liquor to about ½° Tw After six rounds in the sour the valves are raised, and after draining, the goods are well rinsed.

If the lace contains draw threads for subsequent separation of the patterns, the last wash is succeeded by the addition of a solution containing a little white soap, otherwise the goods are scoured off sour, taken to the hydro-extractor and dried sufficiently for handling by the finisher

The above processes appear at first sight to be extremely complicated, but many of the details merely refer to manipulation of the valves which supply the dolly machines with the various detergents, etc

The above method is taken from practice, but the routine is capable of extensive modifications to suit the degree of dirtiness of the fabric Thus, instead of effecting the second scour in the dolly, it may be carried out by way of a soap scald in an open boiling kier On the other hand, the treatment in the dolly may be extended to comprise a grey scour in addition to the initial boil in the kier.

When time is a matter of secondary importance, the first boil is preferably extended, and the chemics reduced in strength, but the most pressing requirement in the treatment of lace goods is undoubtedly the removal of the dirt Nothing but milling and as many and varied processes as possible will effect this end, and the action of the dolly machine is the best known for this purpose.

Instead of the hydro-extractor, it is more convenient and rapid to use a pair of squeeze rollers (fig 178) to wring out the moisture, but the strain on the delicate fabrics is more severe.

Knitted Cotton Fabric.—These goods, being composed of comparatively clean and soft-twisted yarn of a porous and spongy nature, are readily permeated by lyes and chemics, and their bleaching therefore presents little difficulty. In

general, two forms are met with, viz long pieces of tubular fabric or manufactured hosiery and garments

The former can be treated in the rope form and plaited in the kiers, etc ; but, owing to the space they occupy on account of their light spongy and elastic nature, it is preferable to treat them in the roll or in bundles The separate manufactured articles are also treated in bundles, or better still, in bags of knitted webbing, to avoid the uneven effects produced at the places protected from the reagents by the tying bands

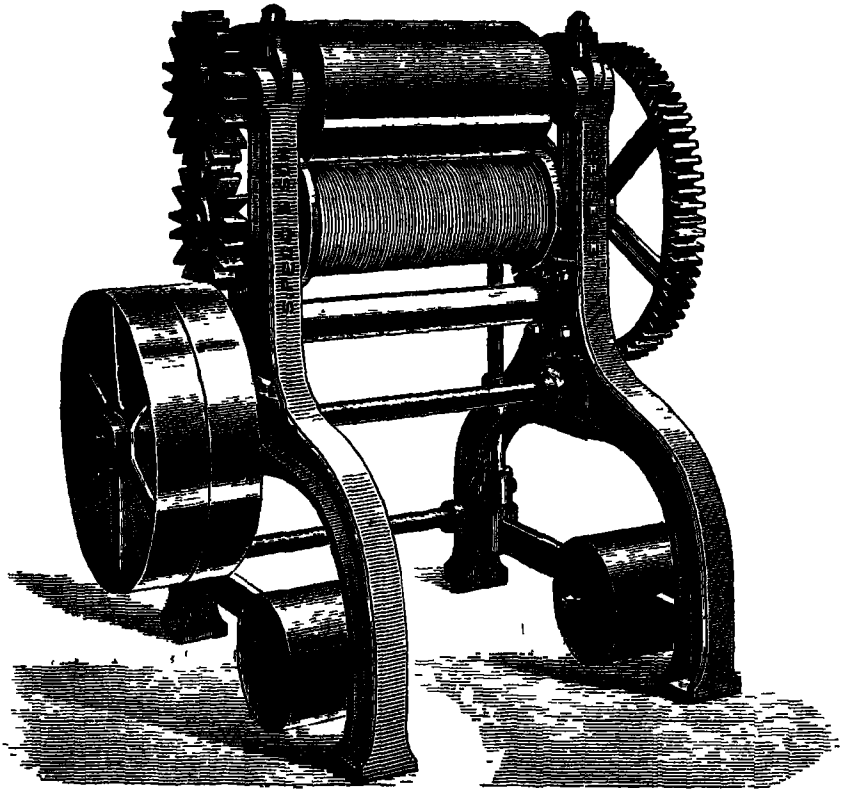


Fig. 178 — Squeezing machine.

The facility with which the liquor may be made to penetrate the goods is illustrated by the fact that it is possible, by careful and even packing, to effect the whole processes of boiling, bleaching, and souring with the intermediate washings, without removing the goods from the kier In this case the kier must be made of wood, and be provided with efficient means of boiling and circulating ; the goods must be tightly and evenly packed so that every part presents a uniform resistance to the flow of liquor, special care being taken to avoid channels. The authors have successfully treated in this way batches of upwards of 50 cwt., consisting of rolls of webbing, placed with their axes vertical, and the interspaces well packed with smaller rolls or loose pieces of similar fabric, the bulk being held down with a framework weighted with stones.

The lye of caustic soda is prepared in a separate tank, which incidentally serves as a water-softening apparatus, and the clear liquor run into the kier till the fabric is immersed and the whole left to steep overnight The necessary quantity of caustic soda is 1½ to 2½ per cent (Na_2O) on the weight of the goods treated, to 560 gallons of water per ton A boil of seven hours duration at low pressure follows the steep, the liquor is then run off and a constant flow of water through the kier is maintained until the effluent is perfectly clear The goods are then left to drain The chemicking process, which follows, is effected by the circulation of electrolytic sodium hypochlorite at 4° for four and a half hours, the liquor is then drained off and the fabric washed as before A souring solution of vitriol at ½° Tw is then circulated for two and a half hours, and a final wash and drain completes the process The goods are then ready for squeezing and drying over drying cylinders or in the stove

It is, however, usually necessary to treat the goods in the dolly or its equivalent with soap suds to remove adventitious dirt

The stationary process above mentioned is a slow one, and dependent on careful packing, any irregularity in this matter inducing liability to grey patches

The commoner and more rapid process consists in treating the goods in bundles or enclosing small articles in porous bags and boiling them in a more open disposition They may be dropped into the kier while the liquor is being added, thus becoming well saturated and settling down into a homogeneous mass through which the lye can be conveniently circulated

After boiling from four to six hours, the goods are rinsed and allowed to drain in the kier, or may be immediately scoured in the dolly with hot water, and then treated, first, with soap-suds and afterwards with water They are then partially dried by passing them through the squeezers (fig 178) or hydro extractor They next proceed to the bleaching tank or cage, as described for lace goods They are afterwards washed and soured, and again washed in the dolly They are treated in the same or a similar machine with a final scour in white curd soap to remove all traces of dirt, and, if necessary, are blued to the desired shade by the addition to the soap of a measured quantity of indigo, smalt, or methyl blue

After a final wash they are dried in the hydro extractor and stoved or boarded and pressed according to the finish required The final treatment with soap in the dolly may be modified to suit the feel demanded The quality of the soap used must be carefully attended to, since it affects the final colour considerably

The dollying machines used for lace are applicable to hosiery, but it is convenient to have a machine with a smaller tub when dealing with very small articles of hosiery

The Hydro-extractor.—A very convenient form of centrifuge or hydro-extractor is Manlove and Alliott's, shown in fig 179 It is built with a self-contained steam engine, and may be set down in any position without regard to line-shafting, etc, and requires only a small steam pipe connection to make it ready for work The whole machine swings on rods, and consequently requires no heavy foundations

Fig 180 represents an under-driven centrifuge of the peg top type The top of the pan has a balanced cover which keeps dirt out of the revolving basket, and also prevents accident while the machine is running The essentials of a hydro-extractor are a cage or basket made of a perforated material connected to a vertical shaft, which gives it a rapid spinning motion in a vertical plane The fabrics are thrown against the side, and the water passes through, and is

collected in the outer cage, and leaves by the outlet pipe. They are extremely useful for small lots of goods which will not stand wringing.

Yarn.—The methods of treating yarn vary in severity, according as they are hard- or soft-twisted, low or high count, Egyptian, Sea Island, or American

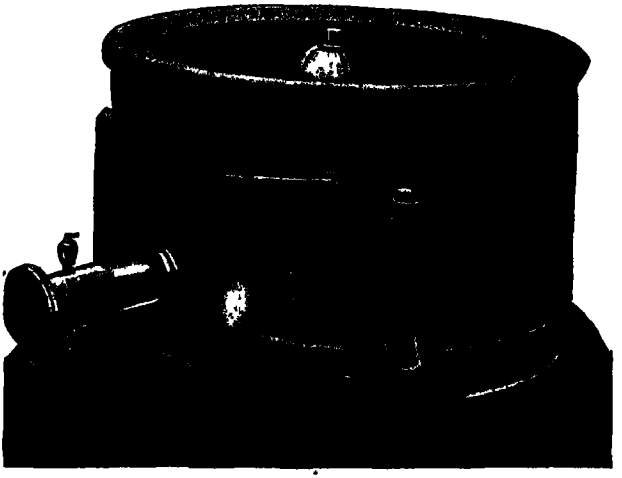


FIG. 179.—Steam-driven centrifugal hydro-extractor

cotton. The amount of cleansing necessary, and the degree of whiteness required (whether half, three-quarters, or full bleach), and whether for dyeing or white shades, also affect the treatment. Fine counts, being necessarily spun from superior qualities of cotton, are the easiest to bleach, but require most

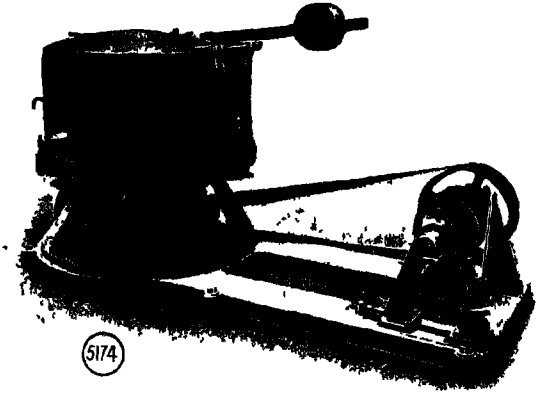


FIG. 180.—Belt-driven centrifugal hydro-extractor

care in handling. The process must also be arranged with due regard to the conditions of strength and weight of the finished product. The lye boil is, as we have seen, the chief factor affecting weight, while the strength is dependent upon the bleach. It is very difficult to get the best whites if a minimum loss of weight is insisted on. In these cases recourse is generally had to blueing, or scouring with soap, to which the tinting material is added.

The simplest process for yarn, and applicable to almost any quality and count of American yarn, is that indicated for the stationary treatment of hosiery, and this, followed by scouring, as above mentioned, is capable of producing the most beautiful whites

In its most rational form the yarn is packed in the kier by hand, so that the

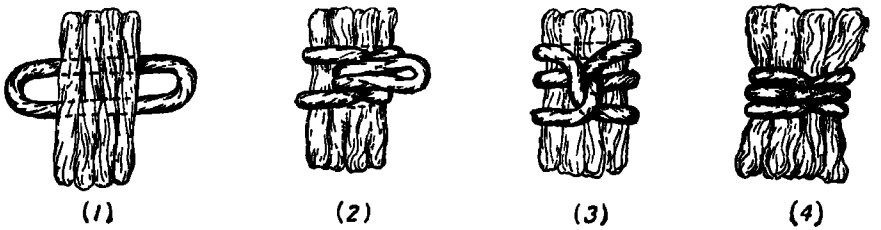


FIG 181 —Yarn in loose bundle

hanks stand endwise It is, in fact, unnecessary to disturb the bundles otherwise than by untying the binding cords, but this assumes very careful packing to prevent channels The usual practice is to untie the bundles in the grey room, and reassemble them in a more open form, utilising one of the hanks as a binder This is done by wrapping the binding hank round the bundle at



FIG 182 —A chain of hank yarn.

right angles to the lie of the hanks, and slipping one end of the hank inside the loop formed by the other, and securing the inner loop by threading it over the end of the bundle, as shown in fig 181.

An alternative method of handling the yarn is to thread the hanks into a chain (fig 182), which can then be conveniently passed about the croft from the boiling to the souring tanks by means of winces in a similar manner to the treatment of cloth in the rope form

The defective feature in both of the above forms is the liability of the knotted portions to become tightened as the yarn swells after damping and during boiling, hence, such portions naturally offer increased resistance to the circulation of the liquor To remedy this the knots are kept as loose as possible, and the bundles rearranged or the chain re-formed, say between the two boils or succeeding processes.



FIG. 183. — One hank bundle or "noddle" for isolating short hank yarn

These methods of tying are only permissible if the length of the hank is sufficiently great, which is not always the case. It then becomes necessary, to prevent entanglement, to twist each hank up into a compact form, in which no separate threads are capable of engaging with those of other hanks (fig 183).

A further device employed when yarn occurs temporarily in a loose state and has to be so handled, consists in giving the threads in a short portion of the hank a spiral twist, and then crossing this twisted portion over itself to form

a "noddle," as shown in fig 184 The hank can then be handled without fear of entanglement of the threads, and be readily opened out again when required

Taking the case of yarn which is formed in the grey room into loose bundles These are wheeled in trucks to the kier and packed, as evenly as possible, either by hand or by dropping them into the liquor, which is entered at the same time as the yarn, thus ensuring its thorough impregnation

When the kier is packed, the contents are loaded at the top to prevent excessive motion during boiling, which would be accompanied by cottering or entanglement of the threads, and mechanical strains and damage

Hard twisted and Egyptian yarns should be first boiled under pressure for seven hours (using 1½ to 2½ per cent of caustic soda on the weight of yarn), rinsed, and removed for a low pressure boil The removal or "turning over" renders the treatment more uniform, and gives an opportunity for slackening or rearranging the binding hanks, as also those parts of the bundle in which these hanks may have restricted the flow of liquor



Fig 184.—Arrangement of hank or noddle" to prevent entanglement during piling

In the case of extremely dirty yarn it is necessary to wash it mechanically between the two boils

After the yarn has been packed in the low pressure kier (as already described), the second boil is carried out at half the strength of lye used in the first, and for four to six hours

The liquor is then run off, the contents are well rinsed and chemicked, rinsed, soured, and again rinsed without removal from the kier

The subsequent treatment is that of soaping in the stocks first to remove the dirt, and then, having rinsed out the soap, to give a finishing scour with white soap, to which is added a measure of tinting blue

The yarn is then removed from the stocks and rinsed in water by hand or by means of the reeling machine (fig 144), and piled to drain or taken direct to the hydro extractor, in which the bulk of the water is removed from the yarn

The next process consists of straightening out the threads preparatory to drying, as the fibres tend to retain the form in which they are dried, and to cling together by reason of the stiffness of the hairs or projecting fibres which rise from the thread when the water is dried out

One end of the hank is threaded over a horizontal post, and through the other is threaded a short staff, which is drawn with a jerk so as to stretch the hank out to its full length Between successive jerks the hank is rotated and opened out and crossed threads rectified, so that it can be finally transferred to the drying pole with the skeins arranged in proper order and the threads well separated, lying even and parallel It is dried in a stove by natural draught, the air rising upwards past steam radiator pipes, and through the hanks, which are threaded over maple wood poles supported at their ends and arranged in tiers

It is important to commence drying without leaving the yarn about in the damp state, and it is equally important not to over-dry the yarn, as not only is the colour thereby impaired, but its physical strength is also affected in a manner that is not entirely remedied by conditioning Moreover, excessive drying introduces an unnecessary risk in respect of the concentration of any residual traces of chemicals from the preceding operations

The methods of boiling and bleaching above indicated are capable of considerable variation in practice, and the scouring in the stocks is frequently omitted. The same treatment may be effected equally well in the dolly machine, but where soaping is omitted the recourse is usually to rinsing either in the reeling machine or in one or other of the special rinsing and blueing machines referred to in the chapter on washing machines

Another method of procedure consists in boiling the yarn in loose bundles in a high-pressure kier and rinsing it in the same These bundles are removed to stone chemic and souring tanks, where these liquors are circulated through the goods, without removal for the intervening wash. The yarn is then washed and blued in a circular reeling machine, the excess of moisture removed by squeezing in a hydraulic press, and the yarn then shaken on the posts to straighten the threads, and stove-dried

A very effective method of inducing perfect circulation of the chemic and sours through the yarn is by means of the vacuum kier already described (see chapters on Bleaching)

Kuehn has introduced a system of bleaching yarn either in the hank, cop,

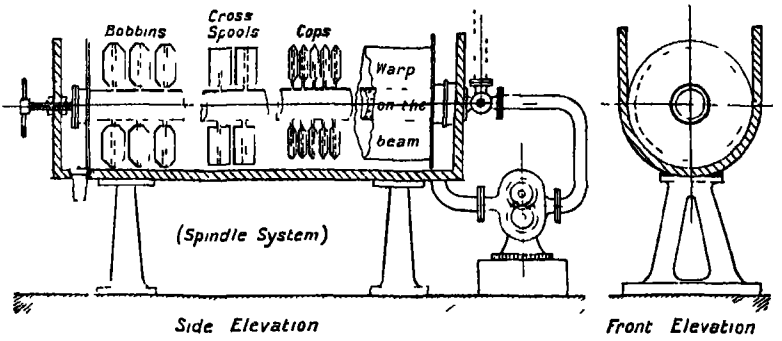


FIG 185.—Kuehn's apparatus for bleaching warps, cops, etc

pirn, or warp, in which it is claimed that the impurities can be discoloured and a full white obtained without recourse to dissolving out the impurities with alkaline lyes His method is to circulate through the cotton a compound bleaching liquor consisting of an alkaline hypochlorite and turkey-red oil The object of the latter is to act as a vehicle for the oxidising agent, assisting it by emulsification to more readily penetrate the pores of the fibre and attack the colouring matter without attempting the removal of the resinous matters It is further claimed that the oil used has a distinct protecting effect on the cellulose, though why this should be is not obvious

The main object of the process is to effect the oxidation of colouring impurities without appreciable loss of weight, strength, and substance of the yarn

The circulating arrangement, as applied to cops, pirns, and warp on the beam, is illustrated in fig 185.

In the ordinary bleaching of warps and chains, the scouring may be effected by either (1) boiling the warp in the kier in the ball form as delivered to the bleacher, a method which is liable to uneven circulation, or (2) plaiting in the kier, or (3) drawing the warp slowly through a machine containing a series of rollers to extend the passage of the warp through the boiling alkaline lye contained in the machine

Two or more warps pass simultaneously through the apparatus, by means of

draw rollers at the delivery end, and thence over a grooved wince into a wagon Thence they are washed through warm water in a similar machine, and enter a pair of squeeze rollers to extract the water They are then plaited into a chemic tank and subjected to circulation of chemic at 5·5° for one hour and allowed to drain

After washing souring, and draining in the same tank they are winced out, washed through warm water in the washing machine, as above, squeezed, delivered to the drying tins, sized, tinted, and made up into the ball as received

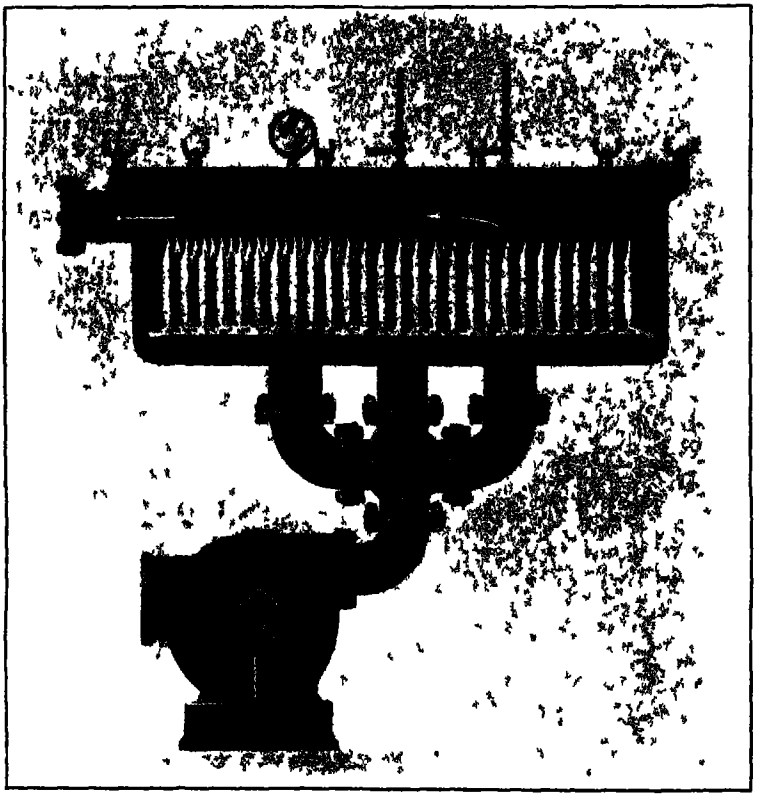


FIG 186 —Apparatus for bleaching cops

The scouring and bleaching of cops, sliver, raw cotton, etc , are effected in the apparatus of L Huillier, Paris, illustrated in figs 186, 187, and 188, the distinction between the treatment of the first named and the latter two being in the substitution for the frame supporting the perforated spindles, of two perforated plates containing between them the charge of material to be treated

The closed vessel is exhausted of air by vacuum and the scouring agent entered and circulated by means of the pump The same method is applicable to washing, while for drying, the vessel is charged with compressed air, so that the wet bobbins become thoroughly impregnated with it The air, impregnated with moisture, is then withdrawn by an aspirating device or vacuum pump,

warm air is next pumped into the chamber, penetrates into the interior of the wet material, and takes up the residual moisture, so that on pumping out the hot air the bobbins are left quite dry.

The bleaching of cotton for surgical purposes and the manufacture of gun cotton is carried out on a large scale both from raw cotton and the higher grades of cotton-waste. The requirements are extreme purity of the cellulose.

According to Kuehn, the preparation of the cotton with an agent, such as castor oil, is necessary to assist in the removal of the natural impurities in the cotton by emulsification, and to assist the alkaline solvent in penetrating the

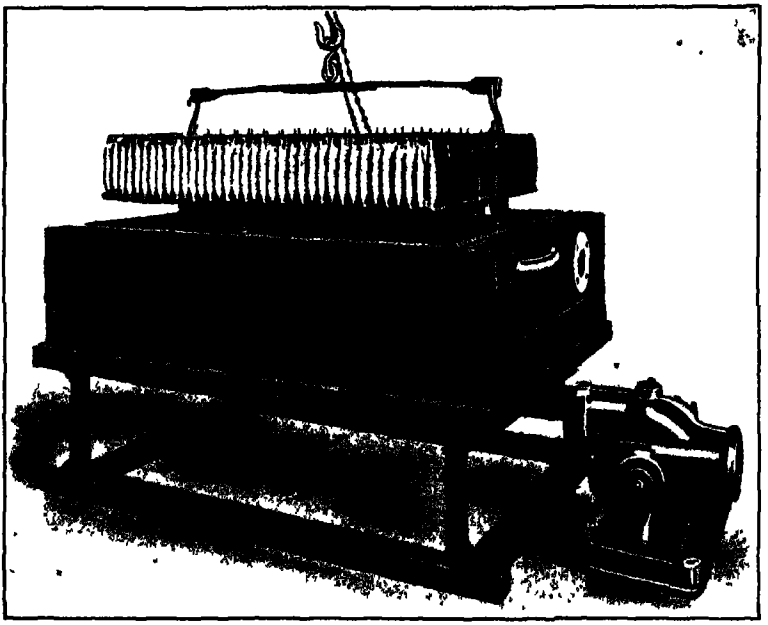


FIG 187 —Apparatus for bleaching cops

cotton fibre The operations mainly adopted in England for treating cotton-waste consist of a preparatory mechanical cleansing of the waste in a willeying machine and passing it pneumatically into revolving kiers or digesters, such as those used in paper mills. Stationary or tipping kiers are also used, and the circulation effected by pump or injector ; but this is liable to interruption through the accumulation of loose material in the working parts

The alkaline solvents used are mainly caustic soda and silicate of soda, the latter on account of its special detergent qualities.

Washing is effected in the beating engine or waste washer mentioned in the chapter on washing-machines ; the wet, loose material is conveyed by brattices or endless belts into and out of the machines.

The chemicking and souring operations are frequently effected without an intermediate wash and with less regard to the non-tendering of the fibre than to the bleaching of the impurities and stains present in the material.

A final wash in the beating engine is followed by drying in the hydro-extractor,

and the material is then fed into the brattice of a hot air drying-machine, through which it is fed from chamber to chamber by a mechanical stoking motion in the opposite direction to the inflow of hot air from a fan and heater

The above is a rough outline of the ordinary process, but it is usually necessary to repeat the boil (which is always conducted at high pressure) and the bleaching

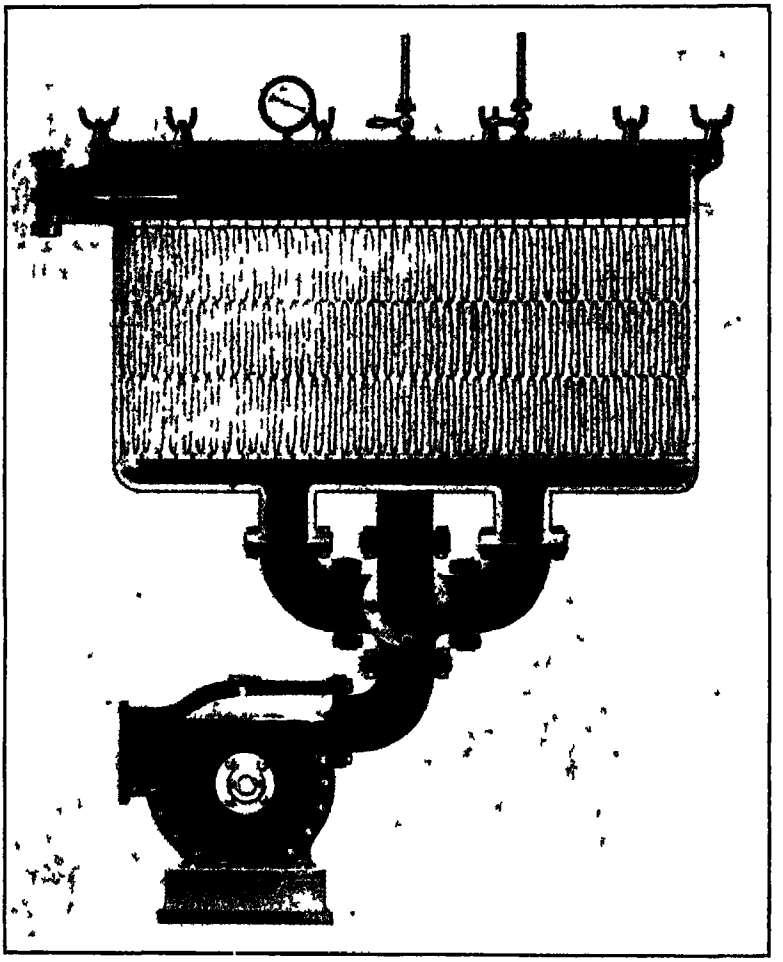


Fig 188.—Apparatus for bleaching sliver

operation Boiling is sometimes preceded by steeping in caustic soda or acid, and if there be much mineral oil to remove, a process of oil separation by benzine or other organic solvent is resorted to

Coloured Goods.—The bleaching of piece goods having coloured headings, stripes, borders, or interwoven coloured patterns requires special precautions to prevent the colour bleeding into the white portions or from being attacked by the various chemicals used These precautions depend upon the degree

of fastness of the dyestuff used or the readiness with which it may be stripped.

Very few dyestuffs which are used for cotton goods are sufficiently fast to allow of the normal bleaching process being used, although certain colours, such as two-bath aniline black, indigo, turkey-red, catechu brown, and buff, allow the cloth to be treated in the normal way. Many of the colours used are so fugitive, or bleed so readily, that a compromise must be effected between the thorough bleaching of the cloth and the retention of the colour. This is recognised by dyers, and the most fugitive colours are applied only to goods requiring the minimum amount of bleaching.

The most scientific way of ascertaining which of the chemical processes are inimical to the retention of the colour is, obviously, to identify the dyeing class to which the colour belongs, and then refer to their known properties and reactions with the chemicals to be used Particulars of the necessary tests may be found in Trotman's *Technology and Bleaching and Dyeing of Textile Fibres*, or A G. Green's *Analysis of Dyestuffs* But this is a long process, and, moreover, the members of the same class of dyestuff differ in their degree of fastness For these reasons the more usual practice is to perform tests directly upon samples of the dyed goods by treating them with the various processes to be used It is thus possible, without recourse to exact chemistry, to determine, by observation of the effects produced on the samples, which processes must be used with caution, and then, confining attention to these, to find out how much treatment, if any, they will stand in modified forms of these particular processes

The following tests for fastness are also useful and are taken from the Colour Index of the Society of Dyers and Colourists Five degrees of fastness are recognised, represented by the numerals 1 to 5. The fastest shade is represented by 1 and the least fast by 5

1 *Fastness to Alkalis* The dyed material is steeped for two minutes in concentrated ammonia and also in 10 per cent soda and dried without rinsing

(1) Unaltered by both ammonia and soda
(2) A little colour is removed by both ammonia and soda, or there is a slight alteration in shade
(3) A little colour is distinctly removed or the shade is altered more plainly
(4) Considerable alteration
(5) Complete destruction of the colour or complete change of colour

2 *Fastness to Soda Boil*—The dyed sample and some white cotton are boiled for half an hour in a soda solution containing 2 grammes of soda ash per litre

Alteration in Shade	Bleeding into the White
(1) Unaltered	(1) Does not bleed
(2) Slight loss in depth	(2) Bleeds faintly
(3) Distinct loss in depth	(3) Bleeds distinctly
(4) Considerable loss in depth or change of shade	(4) Bleeds considerably
(5) Colour destroyed	(5) Bleeds considerably with a change in shade.

3. *Fastness to Washing*—This test is concerned with the loss in depth, or alteration in shade of the dyed material, and the colour of the soap-bath, or the fact of the colour bleeding into the white, is not taken into consideration The dyed material is treated with a solution containing 2 grammes of Marseilles soap per litre for half an hour at 60° C, and also at 100° C. in soft or distilled water

(1) Unaltered at 100° C.
(2) Unaltered at 60° C, slight loss in the depth of the shade at 100° C.
(3) Slight loss of colour at 60° C, considerable loss of colour at 100° C.
(4) Distinct loss of colour at 60° C.
(5) Considerable loss of colour at 60° C, and the colour is stripped completely at 100° C

4 *Fastness to Chlorine*.—The alteration of shade produced by steeping the dyed material for one hour in calcium hypochlorite, sp gr. 1 007, and also in calcium hypochlorite of one-tenth this strength, is estimated—

(1) Unaltered by the stronger solution
(2) Unaltered by the weaker solution, slightly altered by the stronger solution
(3) Slightly altered by the weaker solution, considerably altered by the stronger solution
(4) Considerably altered by the weaker solution, completely destroyed by the stronger solution
(5) Completely destroyed by the weaker solution

No general classification of processes is possible The standard processes must be modified to suit the particular fabric, the modifications required having been ascertained previously by experiment.

The general principles are—

1 Sodium hydroxide is not used except in special cases, but is replaced by the milder sodium carbonate.

2. If colours will not stand the action of sodium carbonate, a light treatment with soap and water may be all the preliminary purification that is possible

3 The time of treatment and the temperature of the scouring liquor are kept as low as possible

4 Preliminary treatment with diastase is often useful, making less scouring necessary

5 The chemics are used more dilute than usual, and are kept on the alkaline side in order to render them less active.

Other modifications or precautions are—

(1) Reduction of the quantity of goods undergoing simultaneous treatment in bulk, and hence increasing correspondingly the rapidity of treatment
(2) Avoidance of mechanical pressure or friction between coloured and uncoloured portions
(3) Suitable disposition of these portions relatively to each other
(4) Increased care in effecting uniformity of action throughout the piece, so as to avoid unnecessary duration of treatment in an undeveloped portion of it at the expense of excessive treatment of parts already sufficiently acted upon

As regards temperature, there are a few colours that will withstand the effect of the temperature incidental to boiling in lime or soda above atmospheric pressure, and none that will stand more than a moderate elevation

Another range will stand normal temperature and concentration of boiling liquors for a short period, and these conditions may be met by the subsequently described process of "hanging out" and separating from the rest of the cloth, either at the commencement or termination of the boil In this respect it may be noted that in the latter case the liquor has, by exhaustion and dilution, arrived at a stage of reduced activity in its power of attacking the colouring matter.

As regards weaker colouring matters, we have, first, the case in which boiling temperature is inadmissible, and a "scald" only is permissible. In the worst cases, the chemical activity of the lye must be reduced until its solvent properties are replaced by merely detergent action, and a soap lye or merely warm water steep remain available, the task of whitening the goods is then largely relegated

to the chemicking and souring process, and even one or other of these may require suppression

Where lime has a prejudicial action, the alternative is a soda or potash boil, the activity of which may be reduced by largely replacing caustic alkali by carbonate or bicarbonate of soda.

It naturally follows that the greater the limitations imposed, the more serious becomes the difficulty in softening and reducing the motes in the cloth, and occasions arise in which this duty devolves on the chemic with the assistance of nothing but a short scald in warm water or a soap solution. The application of a preparatory scald in a weak solution of common salt shows apparently satisfactory results as regards retention of colour, reduction of motes, and whiteness of groundwork The state of the chemic bath is always a matter of great importance when dealing with colours. A disturbing factor, quite irrespective of the adjustment of the concentration of the liquor, arises out of a decomposition of the chemic, which is accompanied by the liberation of hypochlorous acid and chlorine. Its production is apparently connected with the presence in the cloth of impurities which have not been sufficiently removed in the preceding scour. Thus, for example, the presence of sodium chloride, which is sometimes used in dyeing, would, as has already been indicated, cause the reversion of the equation

$$2Ca(OH)_2+2Cl_2 \rightleftharpoons Ca(OCl)_2+CaCl_2+2H_2O$$

Again, many organic colouring matters when oxidised yield acid products, which fix the free lime present in the chemic, and thus assists hydrolysis In some cases the amount of acid which is formed is even sufficient to neutralise the whole of the lime in solution, and then free hypochlorous acid is produced. The effect is more apparent (1) in the first than in the second chemic, (2) in cloth that has been indifferently washed, (3) in a chemicking process in which the volume of liquor employed is small, and (4) when the well has not been recently cleaned out It is also found to increase (5) after the circulation of the liquor has been interrupted and is restarted. The facts mentioned in (1), (2), and (4) show that the occurrences are due to other influences than the mere accidental mixture of chemic and sour, with their usual concomitant, the " buck sour "

This effect is very seldom met with when sodium hypochlorite is employed The safeguard in connection with the use of chloride of lime is the addition of lime water, thus inhibiting the decomposition, whether due to acid products or neutral salts.

Temperature.—The regulation of the temperature of the lyes is best controlled by effecting their circulation and heating separately, instead of using a puffer-pipe or injector in the kier Regular circulation is desirable, because the alternative, or vomiting, action induces movement and contact between the coloured and plain portions of the fabric, which tends to cause transference of colouring matter from one to the other, while undue agitation loosens the colour and produces the effect of " bleeding."

Duration of Treatment.—The headings and adjacent portions of the cloth may be subject to reduced duration of treatment, while giving the full time to the rest of the piece, by the system of " hanging out." This consists in a method adopted by the plaiter of deflecting to the side of the kier and hanging over the edge all loops which contain a heading. He is advised by a signal from the machine-minder of the approach of a heading, and he then throws these loops so that they overlap the edge of the kier sufficiently to avoid being drawn in again by the weight of the cloth that is subsequently plaited above their extensions

which remain in the kier. He ranges them into assortments of different qualities, which may demand different degrees of modified treatment. Some of these headings may be saved by merely disposing of them in layers towards the top of the kier, whereby they escape the pressure of superincumbent cloth that would otherwise impress their colouring matter into the plain fabric Others demand reduced period of treatment, and are placed on the top of the kier, bundled up, and covered with a cloth and withdrawn after, say, two hours. They are then hung over the edge of the kier, and the headings dipped in water, or the lime otherwise washed out The defect of this method is, that the adjacent cloth in the lap containing the heading gets less treatment than the rest of the cloth, and this is the very part which is most exposed in the made-up goods The hanging-out system is also productive of lime stains at the ends, which are very troublesome and sometimes accompanied by tendering The system of hanging out is continued in the bowking, chemicking, or souring processes, according to which of them have the more detrimental effect on the colour. The inconvenient method of hanging out may often be avoided by merely deflecting the loops containing headings towards the side of the kier, but not throwing them over the edge

It is obvious that the separate treatment that is applicable to headings is out of the question for cloth containing more generally disposed patterns, and the above precautions are more applicable to those goods which must be almost necessarily treated in bulk In view of the precaution necessary against mechanical pressure existing between the folds of the cloth, it is desirable to apply the liquors in such a manner that the cloth is comparatively free to float therein, the weight that would have the undesired effect being relieved by the buoyancy of the cloth

When all the above methods of treatment in bulk for even a reduced period and with small lots are unavailing to preserve the colour, one has recourse to scouring in a machine with a weak lye The machine may, for example, be an ordinary roller squeezing machine, the box being fed with hot lye of alkaline carbonate or bicarbonate For greater convenience in the manipulation of the liquor and steam, a long covered trough may be substituted containing a series of winces over which the cloth is passed, either in the open or rope form, through the lye with which the box is filled, and which is heated with a steam coil The cloth is drawn by draw rollers which also squeeze out excess of liquor, and the impregnated cloth is left to soak and drain for a short period A similar machine may be used for washing, chemic, and sours

Having discussed the general principles involved, some special recommendations may be noted.

Walsh (*J. Soc Dyers and Col*, 1919, p 35) makes the following suggestions for bleaching striped cotton piece goods Firstly, only low-pressure kiers should be used and sodium hydroxide replaced by 1 per cent of sodium carbonate, calculated on the weight of the goods But the pieces may be run through boiling solutions of the alkali at 2° to 3° Tw., giving them five or six dips and then squeezing and washing. They are then packed in a kier provided with an external heated and circulating pump and treated with sodium-carbonate solution (containing 1 per cent. of the weight of goods) at 70° C After washing out of the kier, the goods are chemicked, using a weak liquor (say 1° Tw.), avoiding acidification by carbon dioxide by using covered cisterns and adding a little lime water if necessary. After washing, souring may be carried out in the same cisterns The intermediate washing must be very thorough. Washing-machines with deep boxes and at least six nips should be used.

Matthews (*J Soc. Dyers and Col*, 1921, p 236) recommends treatment with

diastase, followed by bleaching with sodium hypochlorite where boiling is inapplicable.

If the colours will stand a fair amount of boiling, it is useful to add a protective agent to the kier Among these are ludigol (sodium-meta-nitro-benzene-sulphonate), anthraquinone sulphonate, sodium bromate, salts of manganese, and sodium bichromate Soap and sodium perborate may sometimes be employed

Weiss (*J Soc Dyers and Col*, 1921, p 122) suggests replacing the ordinary bleaching liquors by potassium permanganate, followed by a bath of sodium bisulphite

The bleeding of indigo dyed threads during bleaching is attributed by Aue (*J Soc Dyers and Col*, 1920, p 150) to the reducing action of dressings in the material during the alkali boil The addition of an oxidising agent such as sodium peroxide to the liquor is suggested Thus a kier liquor of 1·25 kg of sodium peroxide per 2000 litres of water at a pressure of 0 3 atmosphere may be employed without further addition of caustic alkali

The addition of oxidising agents to the scouring bath is protected by many patents Thus the Badische Anilin und Soda Fabrik (Fr Pat 392858, 1908) claim the use of some easily reducible organic compound such as the salts of mono- or di sulphonic acids of anthraquinone or nitrobenzene Meister, Lucius und Bruning (Ger Pat 218254, 1908) add an alkali bromate to the bowking liquor This may consist of a solution of 1 2 per cent (on the weight of the goods) of solid caustic soda, with the addition of from 0 2 to 0 5 per cent of potassium bromate (also on the weight of the goods) The use of a perborate is claimed by Ger Pat 250397, 1910, while chlorates, bromates, manganates, or similar compounds which generate oxygen in presence of oxidisable substances are mentioned by Freiberger in Ger Pat 250303, 1911

The Farbwerke Hochst varies the process as follows The goods are first impregnated with sulphuric acid of 1° Tw and allowed to lie for twelve hours They are then washed and boiled in an open kier with 15 parts of soda ash and 5 parts of sodium bromate to 1000 parts of water for six hours After this they are washed, soured with sulphuric acid (2° Tw) for three hours, again washed, and boiled For the second boil a liquor consisting of 10 parts of soda ash and 3 parts of sodium bromate to 1000 parts of water is used After boiling for five hours, wash, sour again for three hours with sulphuric acid of 1° Tw , and bleach with bleaching powder solution at 1° Tw for three hours, then wash, sour, and wash again

Lumsden, Mackenzie, and Fort (Brit Pat 165198, 1920) prevent bleeding and staining by using solvent extraction, followed by a mild alkali scouring such as boiling with 1 per cent of sodium carbonate in an open kier

The following examples of processes applied to goods containing coloured headings, borders, and stripes are given rather to indicate various combinations and grades of operations taken from practical working, than to rank as rules to be applied without special tests

GOODS WITH COLOURED HEADINGS, TREATED IN ORDER OF FASTNESS

Example 1

Fast black, buff, red (heavy shirtings).

1 Lime boil with hanging out of headings
2 Hydrochloric acid sour, followed by washing Low pressure soda ash and rosin boil and wash
3 Chemic, wash, sour, and wash
Pink generally requires more care and a low-pressure lime boil

Example 2.

Ditto, for Medium and Light Shirtings.

1 Boil nine hours in lime at low pressure with headings placed to one side
2 Wash and chemic at 2 75°. Circulate for half an hour and then allow to remain for two to three hours
3. Wash and sour with acid of about ¾° Tw.
4. Wash into kier and boil seven hours with sodium carbonate and rosin (about 80 lbs. carbonate and 20 lbs. rosin per 50 cwts of cloth). After boiling, wash.
5. Chemic at 2° for half to one and a half hours.
6. Wash and sour at ¼° Tw, and thoroughly wash.

Example 3.

Worsted Headings (Red and Black).

1 Boil for half an hour in lime and wash off in kier Wince out of the kier and wash slowly in washing machine, without tension, pass into wagon
2 Pass by wince into chemic at about 1 5° and circulate for a quarter of an hour Drain and wince into wagon, washing as before
3. Pass into kier and boil for half an hour to an hour with soap and carbonate of soda.
4. Wash again and chemic, sour and wash as before.

Example 4.

Lilac and green require special care in boiling and sours They are either hung out or subjected to only short boils of about two and a half hours. They are then washed and chemicked and again washed, after which they are boiled at low pressure with soda ash After this they are washed, chemicked, soured lightly, and washed Since green colours often fade with acids, the use of sodium hypochlorite is advisable in order to avoid the necessity of souring

Example 5.

Chocolate Headings.—These may be hung out in lime boil and treated as above, or sometimes they may be soaked in salt and water instead of bowking.

Example 6.

Blue.—The following formula is used —

1. Low-pressure lime boil, with hanging out, and wash
2 Sour with hydrochloric acid and wash
3. Low-pressure soda-ash boil (25 lbs. per ton of cloth) for four hours
4. Chemic, wash, and sour with headings hung out, wash.

An alternative method is—

1. Low-pressure lime boil with headings in, but drawn to the side.
2 Wash, chemic, wash, sour, and wash.
3 Soda-ash boil (3 lbs. per ton), with headings to side as before.
4. Wash, chemic, wash, sour, etc.

Example 7.

Orange Headings.

1. Low-pressure soda-ash boil for two hours.
2 Fill up and steep overnight.
3. Wash into chemic (2°), and wash out into kier
4. Boil with 30 lbs soda ash per ton and a little soap at low pressure for half an hour and steep overnight.
5. Wash into chemic at 1 5°, and wash.
For Egyptian cotton a stronger chemic (2 75°) is employed.

Example 8.

Lemon Headings.—Often these will not stand boiling with soda or soda ash or a high temperature. They can, however, generally be chemicked and soured

The following method is sometimes used: The goods are steeped in salt and water overnight and then washed and boiled for about fifteen minutes in soap and water After this they are washed, chemicked in sodium hypochlorite, and again washed.

Example 9.

Borders and Stripes.—Owing to the longitudinal distribution of these over the cloth, the methods employed for headings are not generally available. Since, however, the quality of the goods is generally low the conditions are less onerous. As a rule the quantity treated at once is reduced to sufficiently small dimensions to allow of rapid treatment, and so avoid the risk of the colour striking through to the white fabric. As much of the bleaching as possible is relegated to the chemicking process, during which the goods must be carefully watched to detect and prevent bleeding of the colours, by at once stopping the process

The following are examples of the processes employed:—

Example 10

Red and Black Borders.—Boil for one hour in weak lime and wash in chemic (2°), circulating for fifteen minutes. After draining, wash and sour with sulphuric acid (½° Tw) Then wash again and boil for one hour with soda and soap. Wash with chemic as before, and finally wash.

Example 11.

Black Borders and Stripes.—Boil for one hour with lime at low pressure, wash and chemic (1·5°). Then wash and sour (½° Tw). After washing again, boil with soda ash for one hour and wash Then pass again through weak chemic, sour as before, and wash.

Note—Chemic strength expressed as chlorine contents in grammes of available chlorine per litre.

CHAPTER XXVIII

STAINS, DISCOLORATIONS, AND DAMAGES.

Frequent reference has been made in the preceding chapters to the danger of over-bleaching and to the many kinds of discolorations and damage to which cotton is subject For purposes of reference, it will be convenient to epitomise the more important of these defects No list can be regarded as complete The number of possible causes of damage seems to increase rather than decrease In some cases it is extremely difficult to find any satisfactory explanation of an obvious defect In fact, no problem is more difficult to solve than the tracing of the cause of damage or discoloration in bleached goods

Damage may be of either mechanical or chemical origin, and often the effects of both are similar Thus, it has been noted that "shot holes" caused mechanically in washing are difficult to distinguish from those due to over heating with live steam

The following list includes the more important and common kinds of damage

1 *Mechanical Damage* – This may be produced at any stage, and can only be avoided by careful overhauling of the machines Uneven bowls of a mangle, or any similar defect, are often sufficient to cause extensive trouble The effect of a defective beetling machine has been mentioned also Shot holes may be regarded as a form of mechanical damage

2 *Distortion of pattern*, accompanied sometimes by rupture of the threads, may be traced generally to the accidental use of too strong a caustic lye, or allowing a dilute lye to concentrate in the goods In this connection the danger of putting a concentrated solution of sodium hydroxide into a kier and then filling it up with water has been referred to

3 *Mineral oil Stains* – These are caused frequently by machines Many people think that a moderately light coloured mineral oil is "stainless" This is not the case The only stainless oils are those which are readily and completely saponifiable These may also cause iron stains if they contain much free fatty acid It is almost impossible to remove mineral oil during the ordinary processes Bleaching may cause it to become temporarily invisible, but it works its way up to the surface gradually and causes loss of colour or actual discolorations It may take some time for this to happen This is why most of the complaints are in connection with exported goods Mineral oil can only be removed by means of an organic solvent Localised stains may be milled carefully with a freely soluble soap or with a solution of soap in an organic solvent Milling is assisted sometimes by the presence of a detergent, such as fuller's earth Stains due to tar are even more difficult to deal with than mineral oil stains The addition of sodium oleate or sulphoricinate to the lye is said by Scheurer (*J S C I*, 1903, p 1344) to remove mineral oil Stains caused by lubricants are accompanied generally by iron, *i e* the stain may be due partly to both causes

4 *Lime stains* are due to unremoved impurities owing to bad boiling or plaiting, deficient circulation, too strong a liquor, incomplete souring, or excess of air Lime " burn " is produced by the presence of unslaked particles of lime or magnesia, which subsequently take up water, producing heat and swelling

5 *Iron Stains* —These may be due to rust in the machines, kiers, or pipes, or to the presence of iron in the water or chemicals used Lubricating-oil stains, as mentioned above, are generally ferruginous Blacklead sometimes contains ferric oxide Iron stains are generally reddish brown in colour, though occasionally when due to tannate of iron they are blue black or black Iron can be removed by means of acid Potassium hydrogen oxalate has been mentioned as a good solvent

6 *Lead Stains* – These are rather similar in appearance to iron stains, but have a dull brown colour The lead is generally present as peroxide, which is produced by oxidation during the bleaching process Lead stains are found sometimes in goods boiled in lead lined kiers or which have lain in contact with lead pipes They are very difficult to remove, but may be dissolved by means of a solution of ammonium acetate They are distinguished from iron stains by the fact that they do not give prussian blue when treated with hydrochloric acid and potassium ferrocyanide Neither do they yield a red ash, but a yellowish or white one If this be extracted with ammonium acetate the lead is dissolved To this solution is added a drop or two of potassium cyanide solution, followed by a little ammonia till the liquid is alkaline Some sodium sulphide solution is next added Any brown coloration will be due to lead, since in the presence of potassium cyanide neither iron nor copper give a colour

7 *Discolorations due to Calcium and Magnesium Soaps* —These generally appear only when the goods have been stored They may be due either to gradual dehydration of the soap or to the liberation of its fatty acids by atmospheric carbonic acid or other acids They are due primarily to the use of hard or imperfectly softened water in scouring These discolorations are often diffuse as opposed to local, and are yellow or light brown in colour They may be produced also from ordinary sodium soap used as a softening agent in the finishing mixture In one case examined by the authors goods wrapped in paper acquired in a few months a uniform yellow tint, which was found to be caused by free fatty acids liberated from the soap used in the softening by acid contained in the paper wrapping

8 *Discolorations due to unremoved Cotton Waxes* These are not uncommon in exported goods They are due to incomplete bottoming in the bowking process They are not apparent in the freshly bleached goods, but on storing in a warm, damp atmosphere residual waxes come gradually to the surface, producing brownish stains or discolorations There is no remedy for these except to bowk the goods again Levine (*J S C I*, 1916, p 687) holds that the yellow colour developed on storing or steaming is due to unremoved nitrogenous impurities

9 *Stains due to Bacterial Growth* These have been dealt with in Chapter X They may occur at any stage of the operations They are due to various causes, such as the use of polluted water, insufficient ventilation and washing, want of cleanliness, or the use of decomposed dressing materials

10 *Discolorations due to Chemicals or to Decomposition of Dressing Materials* —The loss of colour due to the decomposition of starches will be described later Blueing materials are sometimes the cause of trouble Thus, ultramarine is decomposed very readily by acids with the production of a brownish colour.

Some of the dyestuffs used in a similar manner are sensitive to either acids or alkalis

11. *Stains caused by Aniline Vapours.*—When aniline is oxidised a mauve dyestuff (Perkin's mauve) is produced. When white goods are kept near others dyed with aniline black, aniline vapour sometimes becomes deposited and oxidised to a pinkish dyestuff. This stain was first pointed out by Pentecost (*J.S.C.I.*, 1909, p. 1180). Higgins (*Bleaching*, p 126) states that he once used aniline oil to take out a tar stain from some goods, and found that other white goods in the immediate neighbourhood developed a pink discoloration.

12. *Tendering and Stains due to Oxycellulose.*—Oxycellulose gradually causes yellowing, but this is accompanied also by tendering The various factors contributing to the production of oxycellulose have been discussed fully. Perhaps one of the commonest is the presence of traces of iron, copper, or other catalyst in the goods Many authenticated examples have been quoted. The authors have traced, on one occasion, tenderness in bleached goods to the brass bowl of a machine which became corroded when not in use during the week-end. In another case, the tendering of cotton shirts when exposed to a tropical sun was found to be due to copper acting as an oxygen carrier Higgins (*J.S.C.I.*, 1911, p. 188) found black stains produced by a blueing mangle to be caused by mercuric chloride, used as an antiseptic in the starch, reacting with the copper of the mangle, and liberating metallic mercury. These, however, were not characterised by tenderness, but were purely discolorations

13. *Tenderness due to Kier Damage*—This is caused chiefly to the exposure of the goods above the surface of the liquor in the kier, and occurs both in lime and soda boiling It takes the form of patches, several inches across, of tender but not absolutely disintegrated cloth merging gradually into sound material. Higgins (*Bleaching*, p 127), describing this, says that it is not due to oxycellulose; it may be caused by the concentrated action of the boiling alkali, through the drying up of the exposed portions, or to the oxidising action of the air in the steam.

14 *Tendering due to Calcium Carbonate or Lime*—Higgins (*loc cit*) says that the crystallisation of calcium carbonate in the fibre may cause mechanical damage. The cellulose shows no chemical alteration, but under the microscope is seen to be profoundly affected. When a deposit of lime is formed locally in the cloth, *e.g* by the drying of exposed portions in the lime boiler, calcium carbonate may be formed inside the fibre. It may be quite tender, and show a large number of kinks or bursts resembling the nodes of bamboo.

15 *Tenderness due to Acids*—This is due generally to hydrocellulose, and is caused by incomplete washing after souring, or to the use of dressing materials containing acids. The use of sulphuric acid to produce scroop is also sometimes responsible for this kind of damage. Acid tendering is often found in unions which have been bleached with sulphur dioxide, and in cotton dyed with sulphur dyestuffs, many of which develop sulphuric acid gradually on storing.

It is not suggested that the above summary is anything like inclusive. There are many cases of damage which cannot be classified, and each of which requires a special investigation

CHAPTER XXIX.

FINISHING AND THE MATERIALS USED IN FINISHING.

After the goods have been bleached and washed, they are transformed from the rope form to the open width and subjected to mechanical processes with the object of correcting strains and twists produced while passing through the croft. They are then dried or partly dried, after which they are ready for finishing

The finishing of cotton goods is largely a physical or mechanical process, but, at the same time, it demands considerable knowledge of the chemicals used. In some cases the processes are entirely mechanical As a general rule the goods are passed through an aqueous solution, or a mechanical mixture or colloidal solution of the bodies which it is desired to apply, and then redried, pressed, and ironed, or otherwise mechanically treated, in order to produce the effect required. The method of applying the finish and the production of the mechanical effects will be described later. The final effect of a finish is to a large extent determined by these mechanical operations, but these can only produce their full and proper effect when the chemical properties of the materials used are understood In the absence of this knowledge, finishing becomes a mere rule of thumb, and is only successful as long as the conditions are normal.

An unsuspected variation in any of the materials used will frequently cause the break-down of an empirical process; but if the variation is known, its effect may sometimes be allowed for Many faults in finished goods may be traced to insufficient knowledge of the finishing materials employed Thus, for example, as will be seen later, careless selection of starch or glue may result in discoloration or tendering of the finished goods or encourage the growth of harmful bacteria or moulds Again, absence of chemical knowledge often fails to prevent the mixing in the same finish of compounds capable of reacting with each other, giving rise to new bodies with properties which differ from those of the interacting compounds

Even when scientifically controlled, it is not an easy matter to produce an unvarying result Having regard to this and the fact that in many cases orders depend almost entirely on the finish, it is perhaps somewhat surprising that so little care is taken in the selection of the materials used, price being frequently the chief factor considered. The use of a poor bleaching powder or alkali only increases the cost of the process by making it necessary to use more, but the employment of bad finishing materials is generally not discovered till after the distribution of the goods, when it gives rise to dissatisfaction and claims for damage

The production of improved finishes is a doubtful possibility unless constructive experiments are carried out under strictly scientific conditions, with the same carefulness that would be bestowed upon a chemical research, accompanied by the accurate recording of results. To add bucketfuls of chemicals to an approximate number of gallons of water is extremely unscientific, and when the composition of the materials, measured by means of a bucket, is also unknown, the reproduction of any given result is a matter of chance only. All finishing

mixtures should be made by weight and recorded, and such variations as water content duly allowed for. The quality of supplies should also be frequently checked by analysis.

The methods employed in making up and applying the mixtures will be briefly described later. The exact composition of the mixture to be used must be determined by a combination of experiment and experience, and even with the same formula, different effects will often be produced in different works. This is, of course, partly due to differences in manipulation, but also largely to the other causes indicated above, viz. want of scientific control. Hence it is not desirable or practicable to give formulæ capable of general application. A very large number of substances are used in producing various effects. They may be classified according to their properties as follows —

1. *Filling materials*, such as gypsum, calcium carbonate, magnesium sulphate, various silicates, and barium sulphate

2. *Stiffening materials*, such as the starches and preparations thereof, dextrin, gelatin, and glue, casein, gums algin, and preparations of Iceland and Irish moss, Carnauba wax

3 *Softening Agents* —Soaps, saponifiable and unsaponifiable oils and waxes.

4 *Blueing Materials* Ultramarine, prussian blue, smalt, and aniline dyes

5 *Antiseptics* Boric acid, borax, copper salts, phenol, formalin, and zinc compounds

6 *Deliquescents* —Magnesium and zinc chlorides and glycerine

7 *Fireproofing agents*, such as metallic oxides, tungstates, phosphates, borates, and silicates

8 *Waterproofing Agents* —Insoluble soaps, oxidised or oxidisable oils, gelatin tannate, formalin gelatin, paraffin wax, ceresin, and rubber solutions

The above classifications are of necessity somewhat general in character and not exhaustive, and relate to the more prominent characteristics of the agents referred to Some of these agents perform additional functions, or may be classed in more than one category

Thus, filling agents, though applied chiefly for the purpose of adding weight or substance to the cloth, exercise their individual effects upon the superficial appearance and the feel of the cloth, even to the extent of developing stiffness therein Deliquescents, and deliquescent antiseptics, are, incidentally, also weighting, and softening or mellowing, in their effects The various agents operate in very different degrees according to their special nature and application This is notably the case with stiffening agents, the effects of which may vary from hard, rigid, brittle finishes to such as are elastic, or apparently as pliable as the natural cloth, and suggest a pure finish In the latter case they are termed assistants They may also act as binding agents for filling materials, or as a medium for the even distribution of the colouring agents In common with other agents, they have the quality of disposing the cloth for the development of various surface effects, such as dullness, gloss, etc

In the following descriptions their finishing qualities are only briefly alluded to, as these are so variously developed by the mechanical processes of finishing, and by their mutual reactions, that for their more detailed treatment manuals on the subject should be consulted

Filling Materials.—French chalk, being finely ground and free from gritty matter, possesses the property, when incorporated in the cloth (with the assistance of a suitable binding agent), of rendering the surface smoother and more homogeneous than is the case with more coarsely grained materials. It also has a lubricating action with respect to the coarser particles of filling materials with

which it may be associated, which not only favours smoothness of surface when calendered, but also tends to somewhat increase the pliability of the cloth.

Mineral white, or gypsum, possesses excellent filling properties for use with cloth which requires a moderate degree of filling, for either hard or medium finishes, and it also serves, to a slight extent, as a weighting agent, but in this respect is inferior to barium sulphate ("barytes"), which is accordingly employed in conjunction with it, when much additional weight is required

China clay is employed to produce the most heavily filled finishes, in which it is necessary to load the cloth to its utmost capacity The tendency of clay finishes is to produce a stiff finish and a rough, or dull, surface effect, though this can be modified by the admixture, in the making, of suitable ingredients, as described.

The commonest of these is ground gypsum, or, as it is frequently termed, "mineral white." For more expensive finishes this is replaced by calcium carbonate or the finely ground siliceous mineral known as French chalk Finally, mineral fillings may be deposited on or in the fibres by double decomposition.

Calcium sulphate occurs in nature as anhydrite, $CaSO_4$, and gypsum, $CaSO_4\,2H_2O$ Satin spar, or fibrous gypsum, alabaster, and selenite are all varieties of hydrated calcium sulphate and have the same composition as gypsum Calcium sulphate is obtained also as a by-product in manufacturing processes, when lime or chalk is used to neutralise sulphuric acid—

$$H_2SO_4+CaCO_3=CaSO_4+CO_2+H_2O$$

Calcium sulphate is a white amorphous substance It is only sparingly soluble, 1 part of calcium sulphate requiring 500 parts of water at 18° C The solubility increases slightly up to a temperature of 38° C and then decreases up to 100° C Calcium sulphate is comparatively readily soluble in a hot solution of hydrochloric acid When gypsum is heated to a temperature of 110° to 120° C. it loses part of its water of crystallisation, crumbling to a powder termed plaster of Paris –

$$2CaSO_4\,2H_2O \rightleftharpoons (CaSO_4)_2H_2O + 3H_2O$$

When plaster of Paris is mixed with about one-third of its volume of water it forms a stiff paste, which sets quickly to a hard, white, porous mass—

$$(CaSO_4)_2H_2O+3H_2O=2CaSO_4\,2H_2O$$

The presence of alum, potash alum, or potassium sulphate retards the rate of setting, but makes the set plaster much harder Keene's cement is a mixture of plaster of Paris with potassium sulphate. When plaster of Paris or gypsum is heated to 200° C the whole of the water of crystallisation is expelled The anhydrous calcium sulphate does not set when mixed with water It takes up water very slowly. Plaster which has been overheated in manufacture is termed overburnt or dead burnt

The calcium sulphate used in dressing is generally finely ground gypsum, but a paste consisting of calcium sulphate prepared by treating a solution of calcium chloride with sulphuric acid, and washing the precipitate with water, is also employed. Ground gypsum has a crystalline structure, while precipitated gypsum is amorphous In some respects artificial calcium sulphate is preferable to ground gypsum. It has a softer feel and is more regular in the size of the particles. Ground gypsum, owing to its crystalline structure, gives a harsher feel to the cloth, the harshness being determined to a considerable extent by the size of the crystalline particles. The fineness of the powder may be judged by rubbing it through a fine sieve.

Ground gypsum is never adulterated, but its composition varies, naturally, with the purity of the mineral from which it is prepared. The chief impurities are silica, oxides of iron or alumina, calcium carbonate, and carbonate or sulphate of magnesium It contains from 19 to 20 per cent of water. The following table shows the composition of some commercial samples :—

	Raw.	Raw.	Burnt.	Burnt.
Silica	4 41	0 98	1 54	0 12
Iron oxide and alumina	1·15	...	2 20	0 52
Calcium sulphate	70 79	79 66	86 88	98·96
Magnesium sulphate	0 52	...	.	..
Calcium carbonate	3 32	...	...	...
Magnesium carbonate	3 60			
Moisture, etc.	16 21	19 36	9 38	0·40

The percentage of moisture is estimated by heating about 2 grammes of the sample in a silica dish on a hot plate to a temperature above 200° C and weighing the residue If a full analysis be required, about 1 gramme of the sample is dissolved in boiling dilute hydrochloric acid and the solution filtered into a 500 c c flask. The residue of silica on the filter is washed several times with hot dilute acid and again with water. It is then ignited and weighed Iron oxide, calcium, magnesium, and sulphuric acid are determined in the solution in the manner described for water.

Precipitated calcium sulphate should be tested for free acid by mixing a weighed quantity with distilled water and titrating with decinormal sodium-hydroxide solution in the presence of phenolphthalein

Kaolin or china clay is a hydrated silicate of aluminium found in large quantities in Cornwall Its composition is—

Silica	47
Alumina	40
Water	13

corresponding to the formula $2SiO_2Al_2O_32H_2O$

It is generally found mixed with quartz or mica produced by the decomposition of granitic rocks (Hurst, *Dictionary of Chemicals and Raw Products*). It is separated from these by a process of levigation. The better qualities of china clay are white amorphous powders of sp. gr. 2·2, the lower grades have a yellowish colour due to the presence of impurities, such as iron These are often improved by the addition of some blue, such as smalt or ultramarine. Good china clay should give no soluble matter when treated with hydrochloric acid. The following examples are given by Hurst —

	Cornwall.	China.	French.
Silica, SiO_2	46·78	51·50	48·37
Alumina, Al_2O_3	39·60	33·76	34·95
Water, H_2O	13·16	10·24	12·00
Potash, K_2O	0·12	1·90	2·40
Ferric oxide, F_2O_3	0·09	1·80	1·26
Lime, CaO	0·07	...	...
Magnesia, MgO	...	0·80	...

China clay contains sometimes an excessive quantity of water, which can be estimated in the usual manner. The presence of calcium would render the sample suspicious If the sample be extracted with dilute hydrochloric acid, the filtrate should give no precipitate when neutralised with ammonia and then boiled with a solution of ammonium oxalate. The colour of a good sample should be a pure white, and the powder should not have a gritty feel when rubbed between the fingers Grit may be detected also by making some of the powder into a thin cream with water, placing it on a sheet of glass and moving another over it

As stated above, low grade samples are sometimes mixed with "blueing" agents to improve their colour. Ultramarine or a coal-tar dyestuff may be used for this purpose Portions of the sample are mixed with dilute solutions of hydrochloric acid, sodium hydroxide, and bleaching powder, and compared with another portion mixed with water only Any change of colour produced may be due to the presence of one of the bodies mentioned

French Chalk.—Various finely ground siliceous minerals are used under the name of French chalk Among these are talc and soap-stone

Talc is a hydrated silicate of magnesia having the formula $3MgO4SiO_2H_2O$ It is a translucent mineral of sp gr 2 5 to 2·8 When ground it forms a white powder with a soapy feel The presence of iron or certain other impurities renders it grey or yellowish in colour The chief impurities are clay, lime, and iron, and their presence greatly detracts from its value Some varieties contain more than 5 per cent of clay and iron The following analyses show the composition of commercial talcs (*J S C I*, 1908, p 64) —

Origin.	Tyrol	Switzerland	Austria	France.	Italy.
Silicic acid . .	62·12	60 85	59·59	50 91	51 23
Magnesia . .	31 15	32 08	32 92	24 86	33 32
Alumina . . .		1 71	1 76	13 19	7 08
Lime . .			0 59	1 82	1 80
Iron oxide . .	1 82	0 09	0 79	2 08	1 89

The surface produced by talc is superior to that of the other mineral fillings. The following is an example of a low-grade talc used in finishing —

Magnesium silicate	78 91
Calcium carbonate	12 96
Alumina	6 00
Soluble matter	2 13

A good sample should be free from grit, blueing materials, and should contain only very little matter soluble in hydrochloric acid

Barium sulphate, $BaSO_4$, occurs native as heavy spar (barytes) It is very dense, having a sp gr of 4 6 It is practically insoluble in water and acids Owing to its insolubility it is largely prepared as a by-product in the manufacture of other bodies Thus, when it is necessary to remove excess of sulphuric acid, either barium or calcium carbonate is commonly employed, the insoluble sulphate being filtered off and washed and dried It is also obtained as a by-product in the manufacture of hydrogen peroxide—

$$H_2SO_4+BaCO_3=BaSO_4+H_2O+CO_2.$$

Precipitated barium sulphate is termed *blanc fixe*. It is generally sold as a

paste, containing from 25 to 30 per cent. of water. Barium sulphate has very marked weighting properties, but its covering power is not very great.

Barium carbonate, $BaCO_3$, is found native as witherite. It is a white powder with filling properties similar to those of barytes, but is not so permanent, since it is attacked by acids.

Satin white is the name given to the precipitate obtained by treating aluminium sulphate with milk of lime. It consists of a mixture of aluminium hydroxide, together with some free calcium hydroxide and calcium sulphate—

$$Al_2(SO_4)_3+3Ca(OH)_2=3CaSO_4+2Al(OH)_3$$

This body is largely used in paper coating and has a great covering power, combined with a high lustre. The quantity of free lime present renders it difficult to use for cotton goods unless previously well washed by decantation According to Traquair (*J.S.C.I.*, 1910, p. 327), the following figures represent the composition of the average commercial product :—

Moisture . .	66–70
$Al_2(OH)_6$ . . .	7–9
$Ca(OH)_2$	6–8
$CaSO_4$	13–17
Alkaline salts	4–6

The same author gives the following relative covering powers of satin white, *blanc fixe*, and china clay —

	Area covered, calculated to Dry Colour	Average Moisture per cent
Satin white	100	65–73
Blanc fixe	50	25–30
China clay	35	5

Fillings produced by Double Reaction.—If a fabric be soaked in a solution of a soluble barium salt, such as the chloride, and then treated with a solution of sodium sulphate, insoluble barium sulphate is precipitated in the fibres, in accordance with the equation

$$BaCl_2+Na_2SO_4=BaSO_4+2NaCl$$

Similarly, magnesium carbonate or silicate could be obtained from magnesium sulphate by means of sodium carbonate or silicate—

$$MgSO_4+Na_2CO_3=MgCO_3+Na_2SO_4,$$
$$MgSO_4+Na_2SiO_3=MgSiO_3+Na_2SO_4$$

Such reactions are used in mordanting cotton for dyeing. Thus, tannate of antimony is deposited in the fibre by treating it successively with tannic acid and antimony tartrate. Double reactions are used also in dyeing cotton with mineral pigments, such as chrome yellow or prussian blue. They are employed largely in the weighting of silk.

Stiffening Materials.—These are used for three purposes, viz.:—

1. To impart a desired degree of stiffness or a particular handle to the finished goods.

2. To act as adhesive or binding agents for filling materials.
3. As size to impart strength to a yarn during weaving

The most important of the substances used for these purposes are the starches and dextrins, but many others, as mentioned above, are used to a limited extent. Softening agents, deliquescents, and antiseptics are commonly included in starch or other stiffening or binding dressings to modify the effect in some particular direction or to prevent deterioration of the goods when stored.

In the following pages the more important of the stiffening and binding agents are described

The Starches, $C_6H_{10}O_5$.—These carbohydrates, as mentioned above, are polysaccharoses. Their molecule is thought to be produced by the combination of a number of molecules of a monosaccharose ($C_6H_{12}O_6$) If n molecules combine, then $(n-1)$ molecules of water are eliminated—

$$nC_6H_{12}O_6 = n(C_6H_{10}O_5) + (n-1)H_2O.$$

Although the percentage composition of starch is represented by the formula $C_6H_{10}O_5$, yet its molecule must be some large multiple of this, n being not less than 100 Brown and Morris give the simplest form of starch as being $20(C_{12}H_{20}O_{10})_5$, which would give n a value of 200

It is held by some chemists that starch is composed of two bodies termed "amylose" (or amylocellulose) and amylopectin Samec and Haerdtl (*J S C I.*, 1921, 272A) found that starch could be separated by electro-dialysis into a highly viscous and electro-conducting fraction (amylopectin) and a non-viscous and non-conducting fraction (amylose), the proportions varying with different starches

Samec states, further, that all starches contain phosphorus (*J S.C I*, 1913, p 102), varying in quantity from 0·012 per cent in tapioca to 0·112 per cent. in potato starch From this he concludes that starch substance consists of a compound of a carbohydrate with phosphoric acid, the whole complex being united with a suitable cation or cations to form a salt of the type $(C_6H_{10}O_5)_n(PO_4)_y K_x$ (where K is the cation), and the molecular weight of starch is said to vary from 77,500 to 260,000

Tryller (*J S C I*, 1920, 829A) also holds the opinion that potato starch contains combined phosphoric acid, present as the potassium salt During manufacture the potassium is replaced by calcium derived from the water used, the dry manufactured product being represented by the formula $(C_6H_{10}O_5)_n OH\ PO_3Ca$, where n has a value of 260 corresponding to a P_2O_5 content of 0·165 per cent This would give a molecular weight of over 40,000.

Karrer, however, states (*J S.C.I.*, 1921, 361A) that estimations of molecular weight based upon the constants of colloidal solutions are probably much too high, since in a colloidal solution single molecules are not present but aggregates of molecules He prepared a methyl derivative of starch with the composition $C_6H_8O_3(OCH_3)_2$

This compound forms a true aqueous solution from which its molecular weight was determined This methyl-starch has a molecular weight in water of from 990 to 1026, or, allowing for inorganic matter present, 1200 at most. From this it was concluded that the starch molecule does not contain more than six dextrose residues

Starch is distributed very widely throughout the vegetable kingdom, occurring chiefly in the grain of cereals, seeds, roots, and tubers. It is laid down generally by the plant to serve as a reserve of food material, often, as in the case of grain

and seeds, for the young plant It always occurs in the form of granules, which have characteristic shape and size depending upon their origin These granules are deposited in certain cells known as "amyloplasts" or starch formers The starch is built up in these cells from soluble and diffusible constituents of the cell sap It is deposited gradually from the periphery to the centre, that is, in the opposite way to which a crystal is formed

Starches have different characteristic shapes and structures depending upon their origin As a rule starch granules have a stratified structure, with a small point or hilum around which the strata are laid down The different layers contain different amounts of water The hilum is always rich in water, and each layer alternately contains more or less water, the outer being the poorest in water and richest in substance As a consequence of the increasing proportion of water from the outside to the hilum, fissures radiating from the hilum to the periphery are often formed If starch granules be soaked in alcohol which abstracts the water, the stratification disappears Starch granules consist of two substances granulose and starch cellulose, together with minute quantities of nitrogenous constituents and oil The starch cellulose occurs chiefly in the outer layers It is much more resistant than granulose, and thus forms a protecting coat for the granules This may be ruptured by boiling water, or by mechanical grinding, and the granulose liberated Starch cellulose is less soluble than granulose Thus when starch is treated with dilute acids or alkalis, the granulose is first attacked and with care it is possible to leave the cellulose behind On prolonged boiling with water the starch cellulose is converted largely into soluble starch But Harrison (*J Soc Dyers and Col*, 1916, p 40) states that there is no difference in composition between the outer and inner layers of the starch granule, although the former is more resistant to hydrolysis From the point of view of the bleacher and finisher the more important starches are wheat, maize, rice, potato, cassava, tapioca, and sago The first three of these are cereal starches, potato, cassava, and tapioca are derived from roots or tubers, while sago is prepared from the pith of trees The sago tree or palm is cut down and split lengthwise The pith is removed and powdered The powder is then washed with water to separate the starch granules from the woody tissue The mixture of starch and water is passed through a fine sieve and then allowed to stand for the starch granules to settle The sediment is washed several times and then dried, when it is known as "sago flour" Granulated sago is made from sago flour by making it into a paste with water and drying over a fire so as to partly gelatinise the starch granules and cause them to stick together

Tapioca and cassava are obtained in a somewhat similar manner from the tuberous roots of the manihot or cassava plant, both of which are natural to South America

The Preparation of Starch.—The raw material, whether grain or tuber, consists of a mixture of carbohydrates oil, nitrogenous substances, and mineral matter This is seen in the following table –

	Wheat	Maize	Rice.	Potato	Cassava
Water .	14 5	14 5	14 6	75 5	5 2
Starch .	69 0	64 5	76 0	20 7	68 5
Oil .	1·2	5 0	0 5	0 2	0 5
Albuminoids .	11 0	9 0	7 5	1 9	2 5
Mineral matter	1 7	2 0	0 5	1 0	2 1
Cellulose, etc	2·6	5 0	0 9	0 7	21 2

The problem of the manufacturer is to remove as much as possible of the oil, albuminoids, non-starchy carbohydrates, and mineral matter without losing or damaging the starch When well prepared, starch is almost pure, as shown by the following analysis of a commercial sample of maize starch —

Water	10 50
Soluble matter	0 02
Mineral matter	0 10
Starch	89 38

Owing to the chemical inactivity of starch, it is very difficult to manufacture it by chemical methods, and the older processes were entirely mechanical With the advance of chemical knowledge chemical processes have been gradually introduced, and modern starch manufacture is a combination of the old mechanical with the newer chemical processes The older processes will now be briefly described as applied to the preparation of wheat starch In one process the grain is steeped in water till it becomes soft It is then ground between rollers and again allowed to stand in contact with water, when natural fermentation sets in, with the production, among other things, of lactic and acetic acids These gradually disintegrate the cellular structure of the grain, dissolving the albuminoids and setting free the starch granules These settle to the bottom of the tank, and the solution, containing decomposed or peptonised gluten, is run off and more water admitted, together with a little of the old liquor to start fermentation The process is continued till all the gluten has become soluble and, as far as possible, washed away Of course during the process some of the starch is also attacked and removed in solution, as sugar or dextrin. After the separated starch has settled the supernatant liquid is drawn off and the upper layers of the deposit are removed, since these are less pure, for further treatment The residue is then washed several times with water and allowed to settle The sludge is then removed and drained in linen bags till it is firm enough to cut It is then exposed to the air till air dry, or gently heated in a stream of warm air, being often finished in an oven Another method, in which fermentation does not play so important a part, is the following The wheat is ground to flour and made into a dough with water This is then washed in a stream of water, the starch being carried away mechanically The stream flows through a fine sieve and is continued till the water ceases to appear milky as it runs away The mixture of impure starch and water is then allowed to ferment, or fermentation is artificially induced, to separate the remaining gluten, after which the starch is finished as described above It is obvious that these processes, depending as they do upon bacterial changes, must give a product liable to contain products of disintegration, along with putrefactive and acid-forming bacteria, which will subsequently develop under suitable conditions The starch made by these processes does not exceed 50 per cent of the flour employed While suitable for some purposes, it is unsuitable for others, owing, chiefly, to the imperfect removal of the gluten, which renders the product liable to be attacked by moulds, etc , and often spoils its colour The principle of the washing process is still made use of with mechanical modifications and improvements The following are examples of apparatus designed to facilitate the removal of starch by washing Inverted cones and rotating cylinders are among the most favoured forms of washers In the following process (Fr Pat 328293, 6th January 1903) the raw material is ground, suspended in water, and passed through a series of inverted cones in which the non-farinaceous matter is deposited at the bottom, the starch taking an intermediate position and the water collecting in the upper part The starch layers are separated and washed and again

passed through the separating cones, the process being repeated till pure starch settles at the bottom of the cones. It is then removed and dried The process of *Murdoch* (*J S C.I.*, 1903, p. 153) is founded on the same principles. The apparatus is shown in the diagram, fig 189. The macerated material and water gravitate successively through a series of inverted conical vats provided with open apices. The material is led into the highest vat, and a tank receives the discharge from the apices of the others Two or three sets of tanks are provided, and the precipitate from the first set is collected and passed through the next series; the product is afterwards passed to a tank where it is chemically treated, *after which it is collected and dried*

Uhland's apparatus (Eng Pat. 14428, 1900) also makes use of an inverted cone (fig 190). In the centre of this is a vertical pipe, which increases in diameter as it descends. The mixture of starch and water passes down this

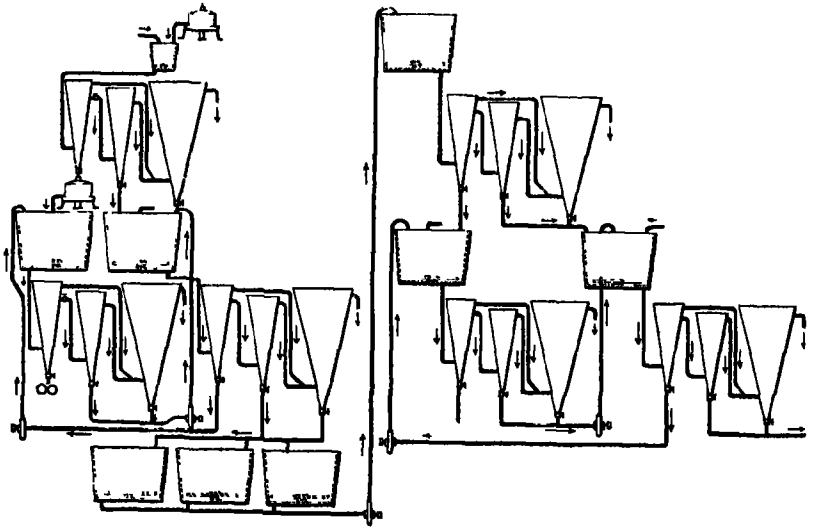


Fig 189

pipe, and at the bottom it is radially deflected by means of a distributor The liquid thus ascends in a vessel of increasing sectional area, and in so doing loses velocity to such an extent that the action of gravity overcomes the motion of the fluid Thus the starch gradually settles, the water passing on and overflowing at the top of the vessel. The starch is drawn off through a cock at the bottom of the cone.

The chemical means of treating starch-bearing materials chiefly depends upon the saponification of oil and the solution of albuminoids by means of dilute alkalis or the disintegration of the structure by means of sulphurous or other acids. Oil, as is well known, is converted by caustic alkali into soap, which is soluble in water and partly removed by emulsification in the presence of alkali. Albuminoids, as a rule, dissolve in caustic alkalis owing to the formation of soluble compounds Starch, while readily attacked by strong alkaline solutions, is not affected by very weak ones Sulphurous acid has the power of loosening the cell walls and liberating the starch, at the same time inhibiting putrefaction and bleaching the starch. Sodium chloride has been proposed by Klopfer (Eng.

Pat. 11159, 1907) as a loosening agent, especially in the manufacture of wheat starch. The flour is mixed with water containing 1 per cent. of salt, which loosens the cellular structure sufficiently to allow of the separation of the large starch granules, this being afterwards completed by centrifugal action, which drives the large granules to the periphery, whilst the small granules and gluten are drawn off as a fluid mass from the middle of the apparatus. This pulp is mixed with water and the smaller granules removed by sedimentation, two qualities of starch being thus obtained.

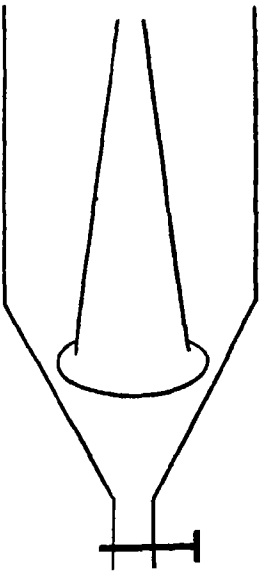


Fig. 190.—Uhland's apparatus.

The Alkaline Process.—A dilute aqueous solution is generally employed, although an alcoholic solution accompanied by subsequent recovery of the spirit has also been suggested. A secret process is, according to Archbold (*J. S.C. I.*, 1902, p. 5), used in America in the manufacture of maize starch, depending on the fact that maize contains two albuminoids, one of which is similar to diastase and soluble in water, while the other, which is identical with gluten, dissolves readily in dilute aqueous caustic soda.

Sulphurous acid not only assists in the disintegration of the grain, but also prevents the growth of putrefactive organisms and bleaches the material. For certain purposes, such as cotton-dressing and laundry work, it is very necessary to remove the last traces of acid. Damage is often caused by acid starches. The acid can, of course, be removed by means of sodium carbonate, followed by washing with water.

Starch may also easily be bleached, if necessary, by means of potassium per-

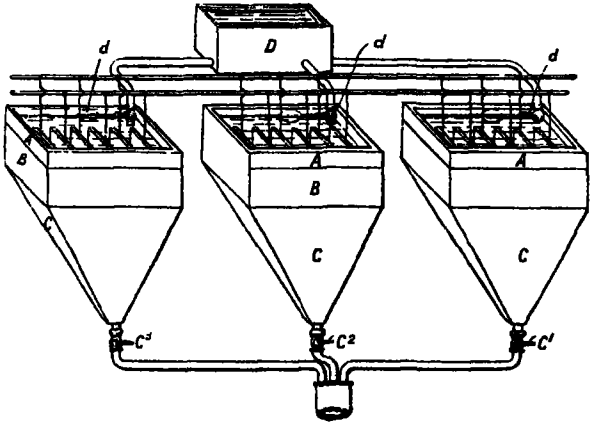


Fig. 191.

manganate in the presence of dilute sulphuric acid, but the same care must be taken to remove the last traces of the bleaching agent. A considerable amount of purification may also be effected by means of *electrolysis*, a principle which is

adopted in the following process (Eng. Pat. 3930, 15th February 1902): The material is steeped in a solution of sulphurous acid, then washed several times with water and ground It is then sifted and the starch deposited and purified on inclined planes, collected, and mixed with water. The mixture is then subjected to electrolysis in the vessels shown in fig 191. Each electrolyser consists of an upper part, A, an intermediate part, B, of wood or other non-conducting material, and a lower part, C, of inverted, truncated, pyramidical form, provided with a tap C_1. The electrodes are connected either in parallel or in series The liquor enters from the tank D, the level in the electrolysers being maintained by ball taps. It flows slowly through the electrolysers and

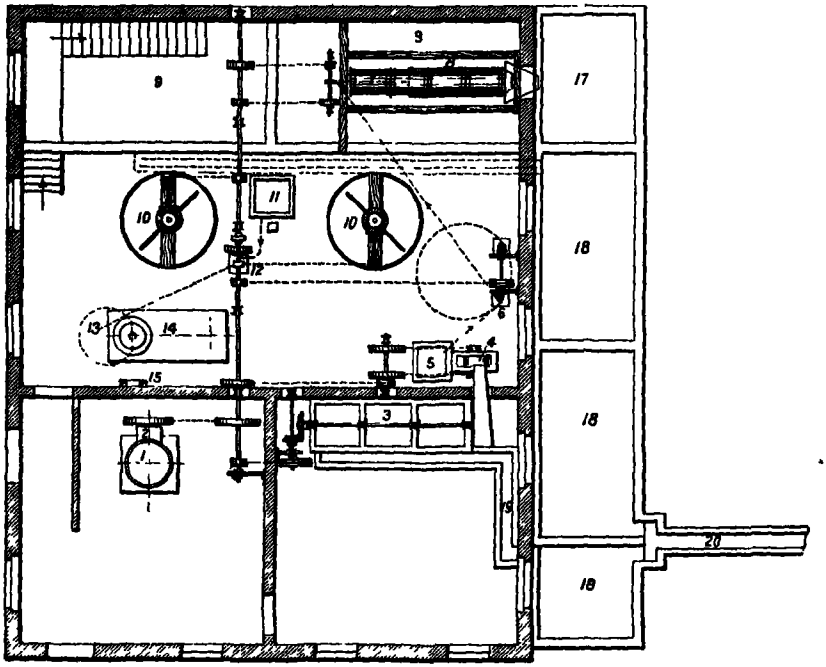


FIG 192.—Plans for starch factory for Irish potatoes or cassava. 1, boiler; 2, engine, 3, root washer, 4, grater, 5, grater tank, 6, pump from grater tank to sieve, 8, shaking sieve, 9, starch settling tanks; 10, stirring tanks, 11, milk tanks, 12, milk pump, 13, centrifugal tank, 14, centrifugal, 15, starch elevator, 17, pulp tank, 18, outside settling tanks, 19, water from washer, 20, overflow to irrigation.

passes through the cocks C_1, C_2, C_3 on to a very fine sieve, which arrests the organic precipitate formed by the electrolysis The product is then sifted and the starch deposited and purified on inclined planes, after which it is dried and stored.

Maize starch is largely prepared by *Archbold's process* (*J.S.C.I.*, 1902, p. 4)

The grain is passed through a magnetic separator, after which it is soaked with water containing sulphurous acid or other antiseptic at 65° C till it is soft. It is then crushed and the germs separated from the perisperm by flotation, the germ, being lighter, floating and the husks sinking To aid the separation the specific gravity of the liquor is kept at 12° Bé. by means of calcium chloride. The germs are collected in a centrifugal machine and dried. The corn is then

ground with water and allowed to settle in a conical separator. The mixture enters at the bottom, and, owing to the increasing diameter of the cone, the velocity is continually decreasing, so that sedimentation takes place The impure starch is drawn out through a cock at the bottom of the cone and clear water issues from the top. The impure starch is then treated with dilute alkali, to remove fat and albuminoids, and is afterwards passed through the cones again, then thoroughly washed with water and the liquor allowed to settle The sediment of starch is then cut into blocks and dried.

Cassava Starch —The cassava root yields a starch of high value at a lower cost of production than maize. In manufacturing the starch (Archbold, *J S.C I.*, 1903, p. 64), the roots are washed with water in an inclined trough (fig 192) in which an Archimedean screw continuously revolves, the roots entering at the lower end and being carried up by the screw against a descending stream of water. The washed roots are then mechanically transferred to a grater, consisting of an upright cylinder with three compartments provided with saw-like teeth The roots leave the grater in the form of a pulp and fall into a conical iron separator, in which the pulp meets an upward flowing stream of water, which carries the light starch with it through a wire gauze diaphragm in the upper part of the separator. The milky fluid containing starch in suspension now passes into settling cones, which it enters at the bottom. As it rises, owing to the decreasing velocity caused by the increasing section, the action partly causes the starch to gradually settle, and only water flows from the top of the cone (see fig. 190). The impure starch is withdrawn through a cock at the bottom of the cone and is treated with alkali, after which it is passed through shakers, and once more through the separating cones The purified liquor then passes into tanks, where it is allowed to settle, the bulk of the water is removed from the sediment by means of a vacuum pump, after which the mass is cut into blocks and dried in the same way as maize starch.

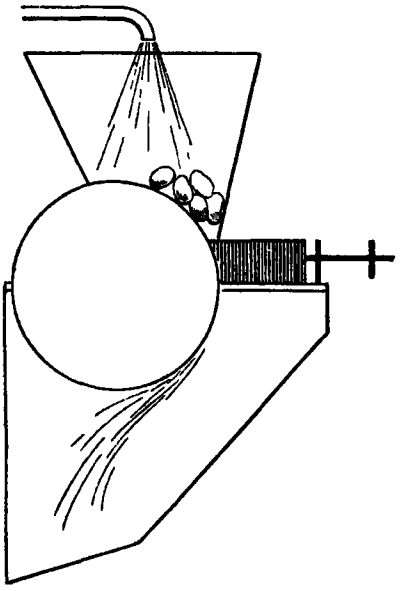


FIG 193

Potato Starch —The potatoes are washed in a similar way to the cassava root and pulped in a rasper, which makes about 600 revolutions per minute, as shown in the figure (fig. 193).

The pulp from the rasper passes to a separator, consisting of a trough, the bottom of which is made of wire gauze of $\frac{1}{60}$-inch mesh The trough is inclined and is continually shaken The pulp enters at the top of the plane and is gradually shaken to the bottom, being subjected all the time to jets of water from a series of taps placed above the troughs. The starch passes through the gauze and is received in large tanks, where it is allowed to settle. The sediment is placed in a second tank provided with a revolving stirrer, where it is mixed with water and again allowed to settle. As it settles it separates into two layers, the lower containing the pure starch The upper layer is rewashed and the lower one taken at once to the

drying tables and subsequently to the kilns heated by steam coils The kiln contains a number of platforms above one another, and is heated by a current of air which passes over steam coils placed beneath the lowest platform. Before passing the steam coils, the air passes over cold-water pipes, where it deposits most of the moisture. With the exception of the bottom one, the platforms are provided with slits through which the starch can be raked on to the next till it reaches the bottom one. The starch is placed on trays and is put in at the top; after a time it is raked through the spaces and falls on to trays on the second platform, and so on, till it reaches the bottom, where it is withdrawn. This arrangement ensures that the wetter the starch is, the lower the temperature of drying Thus, when the starch reaches the bottom floor it has already lost most of the water, and there is no longer any danger of gelatinisation

Properties of Starch.—Pure starch is a white, odourless, tasteless powder consisting of granules of definite size and structure. It is insoluble in cold water and in all organic solvents When it is ground with a pestle and mortar for some time, particularly in the presence of fine sand, the granules become broken down, and a variety of "soluble starch" is produced which is slightly soluble in cold water. Air-dry starch contains about 18 per cent. of water corresponding to a hydrate of the composition $C_6H_{10}O_5\ 2H_2O$ Its specific gravity varies from 1·620 to 1·648

This hydrate parts readily with one molecule of water, forming a monohydrate, $C_6H_{10}O_5\ H_2O$, corresponding to a water content of 10 per cent The monohydrate becomes dehydrated at 100° C or at a lower temperature *in vacuo*. Commercial starches contain, as a rule, from 10 to 14 per cent. of water. Prolonged drying *in vacuo*, or by means of a dehydrating agent, causes a gradual increase in the solubility in cold water, owing probably to conversion of the starch into dextrin.

The change from hydrated to anhydrous starch is accompanied by a considerable increase in its stiffening power If a paste be made with ordinary hydrated starch and with an equivalent quantity of the same after drying, it will be found that the latter has a greater stiffening power even after allowing for the water which has been lost during drying

The Action of Heat.—When starch is heated to a temperature of about 210° C it is changed slowly into, first, "soluble" starch, and then into dextrin This change is accompanied by the production of a yellow or brownish colour If the temperature be raised above 210° C. decomposition takes place and the starch is charred. At still higher temperatures, in the presence of air, the starch ignites and burns with a luminous flame

The Action of Water.—When starch is mixed with cold water and the mixture is heated, gradually, with stirring, it thickens, and, if the heating is continued, changes into a semi-transparent paste or jelly. At the point of thickening, the starch granules will be found to have swollen up to a large size As the temperature is raised, the swollen granules burst and their contents form a colloidal solution with the water The starch is now said to have "gelatinised." When the gelatinised starch is heated for some time, at a temperature of 100° C, it becomes clear and transparent. If excess of water be present it forms a viscous colloidal solution, if only a comparatively small amount of water be present a clear jelly or a viscous liquid is formed. When this hot colloidal solution cools, the mixture sets to a gel known as "starch paste."

The temperature at which gelatinisation takes place varies with the nature of the starch. The following table gives the gelatinising temperatures of some commercial samples.—

Potato starch	65° C.
Wheat starch	70° C.
Maize starch	70° C.
Rice starch	75° C.
Tapioca starch	75° C
Sago	72° C.

Different kinds of starch not only have different temperatures of gelatinisation, but, also, varying capacities for taking up water Thus, potato starch gives a much stiffer paste than sago under the same conditions. But, for a particular starch, the quantity of water required to make a paste or jelly of a given consistency is fairly constant.

The use of starch in the textile industries depends entirely upon its power of forming colloidal solutions when heated with water Starch differs, however, in some respects from other colloids As a rule, the viscosity of a colloidal solution increases, with time, up to a certain maximum Starch paste or gel, when made with water alone, acts differently. The viscosities of its solutions vary with the origin of the starch, but are approximately constant for the same starch MacNider (*J. Ind. and Eng Chem*, 1912, p 417) gives the following values for solutions containing 12 grammes in 30 c c of water —

Potato starch	14 31
Maize starch	2 49 to 2 86
Cassava starch	3 88 to 3 97
Wheat starch	1 24 to 1 26
Rice starch	1 00

But the viscosity falls quickly if the solution be kept Stocks (*First Report on Colloidal Chemistry*, p 47) prepared a 2 per cent solution of potato starch Taking the viscosity of water as unity, the starch solution gave the following figures —

Freshly prepared solution	106 7
After 5 minutes	96 3
After 40 minutes	19 3
After 18 hours	1 3

This decrease in viscosity is accompanied by a gradual deposition of insoluble starch, and the separation of a clear liquid layer containing soluble starch and capable of being filtered In fact, a starch paste or gel always changes, on standing, into two portions, viz (1) a liquid portion containing little starch, and (2) a solid portion containing more starch and less water. This change is termed coagulation It can be controlled or inhibited by various chemical means In general, acids tend to cause coagulation, and alkalis the reverse effect That is, it depends upon hydrogen-ion and hydroxyl-ion concentrations

Since any particular starch behaves consistently when heated with water, its quality may be judged from this property For this purpose 5 grammes of the starch are made into a cream with a little cold water and poured, with constant stirring, into 100 c c. of boiling water. The paste is then allowed to cool, and the weight it will bear without breaking is measured. An instrument suitable for this purpose is shown in fig. 195. The weight of this is, of course, fixed The rounded end is supported vertically upon the paste, and shot is poured into the cup till the end either breaks the surface or sinks to a given mark. The shot is then weighed and added to the weight of the instrument.

For the same starch the stiffening power really depends upon the completeness of gelatinisation. If for any reason the granules do not burst and gelatinise,

loss of stiffening power results Harrison (*J. Soc Dyers and Col*, 1911, p. 84) makes use of this fact to determine the stiffening power in the following manner One gramme of the starch is suspended in 100 c c of cold water and heated, with careful stirring, to a temperature just above its gelatinising point The mixture is then cooled and centrifugalised in a tube graduated to one tenth of a cubic centimetre The ungelatinised granules are thus separated, and their volume is inversely proportional to the stiffening power of the starch

Prolonged boiling of starch with water, or heating of a starch jelly to 100° C, changes it gradually into a modification known as soluble starch which, although colloidal, has no longer the power of setting when its solutions are cooled Starch paste is said to become 'thin" when heated with water, and the longer it is heated the thinner it becomes Naturally this change is accelerated by raising the temperature above 100° C

Harrison and others have succeeded in preparing starch almost free from mineral matter by repeated freezing of its solutions This starch formed only a heterogeneous mixture with water, even when heated, and on standing settled out rapidly This appears to indicate that colloidal solutions are only formed in the presence of electrolytes

Starch is precipitated from its aqueous solution by alcohol, or an ammoniacal solution of lead acetate, or by formaldehyde Tannic acid gives a white precipitate which dissolves on warming, but again appears on cooling If a solution of starch be saturated with barium hydroxide the carbohydrate is completely precipitated as an insoluble adsorption compound

The Action of Alkalis on Starch.—Alkalis act upon starch in four ways

1 They lower the temperature of gelatinisation
2 They inhibit or retard the coagulation of starch solutions
3 They convert starch into the soluble form
4 They are adsorbed, forming unstable compounds, some of which are insoluble in water

The degree and rate of action depends largely upon the hydroxyl ion concentration, *i e* strong alkalis, such as sodium hydroxide, which have a high hydroxyl ion concentration, are much more active than weak alkalis, such as borax, with a smaller hydroxyl ion concentration

The strong alkalis gelatinise starch at ordinary temperatures If potato starch, for example, be stirred into a cold 1 per cent solution of sodium hydroxide, the mixture quickly becomes thick and ultimately swells up to a clear transparent jelly The rapidity and completeness of the gelatinisation is directly proportional to the concentration of the solution of sodium hydroxide up to a maximum of 2 5 per cent If the temperature be raised, the quantity of alkali necessary to cause gelatinisation is decreased till at 100° C even traces are sufficient to produce a considerable effect Alkalis are said to thicken" starch paste just as boiling " thins " it

When a small quantity of sodium hydroxide is added to a starch solution, it not only causes it to thicken, but it tends to make the paste or solution more permanent, *i e* to retard the rate of separation into liquid and solid fractions

Whether or not a starch jelly is formed depends upon the proportions of water and starch present If a little starch be used and sufficient sodium hydroxide, a viscous solution is formed When equal quantities of the different starches are dissolved in the same strength of sodium-hydroxide solution, it will be found that the solutions have different viscosities The viscosity of the same

starch is, however, constant under the same conditions. Ermen has proposed to base a method for the testing of commercial starches upon this fact

Ermen's method (*The Materials used in Sizing*, p 8) is as follows 3·5 grammes of starch are washed into a 250 c.c graduated flask with the aid of 230 c c of cold distilled water, 15 c c. of accurately standardised 10 per cent sodium hydroxide are then run in rapidly from a burette and the flask is filled up to the mark with distilled water It is then shaken gently and continuously until the starch is dissolved, after which it is allowed to stand for twelve hours. The viscosity of the solution is then measured by means of a suitable viscosimeter The tests must be carried out at a standard temperature, as the viscosity of a solution varies with its temperature

If starch be heated for some time with a solution of sodium hydroxide it is converted slowly into a mixture of soluble starch and dextrin, this change being accompanied by the production of a brown colour At the same time decomposition takes place Starch, soluble starch, dextrin, and other carbohydrates are all decomposed by boiling with caustic alkalis, with the splitting off of acetic acid

It is probable that when starch is treated with a cold solution of sodium hydroxide, an adsorption compound similar to alkali cellulose is formed, for in the presence of carbon bisulphide xanthates similar to viscose in properties are formed

When a solution of starch in sodium hydroxide is treated with excess of alcohol, an amorphous precipitate is produced which contains starch and adsorbed alkali If the precipitate be filtered off and dried at a low temperature it has an alkaline reaction and swells up, forming a paste with cold water, which is in every respect similar to a mixture of starch and potassium hydroxide. If the precipitate be extracted, in a continuous extractor, with boiling alcohol, the adsorbed alkali is gradually removed But, according to Tollens, definite chemical compounds are formed with sodium and potassium having the formulæ $C_{24}H_{39}O_{20}K$ and $C_{24}H_{39}O_{20}Na$ The hydroxides of barium, strontium, and calcium are also adsorbed, but the compounds formed are insoluble in water. Hence, when a solution of starch is treated with excess of barium hydroxide it is completely precipitated The composition of the precipitate appears to vary with the conditions of experiment Dextrin is not precipitated by barium hydroxide, and it may be separated from starch in dressing mixtures by taking advantage of this fact About 1 gramme of the starch is heated with a little water till completely gelatinised, 50 c c of a saturated solution of barium hydroxide added, and the mixture made up to 100 c c. and filtered An aliquot part of the filtrate is evaporated to dryness in a weighed dish and the dry residue weighed The dish is then ignited and the ash weighed The difference between the two weighings gives the dextrin present in the volume of the filtrate taken Weak alkalis, such as ammonium hydroxide, sodium carbonate, and borax, gelatinise starch only at high temperatures. They cause thickening even in small quantities, and are used for this purpose in dressing and sizing mixtures

The action of alkalis upon starch is of considerable technical importance, since it forms the basis of the manufacture of vegetable glues. It may be used also for the preparation of dressing mixtures. The starch is made into a cream with cold water and stirred into a solution of sodium hydroxide. Or the sodium hydroxide is poured into a suspension of the starch After gelatinisation is completed, dilute acid is stirred into the mixture till its reaction is neutral to litmus-paper. In this way colourless transparent dressings may be obtained

of any desired consistency. Such mixtures are more completely gelatinised than those prepared by merely heating starch with water.

The Action of Salts.—Many metallic salts act on starch in the same way as alkalis, *i e.* depressing the temperature of gelatinisation. Concentrated solutions of zinc chloride, calcium chloride, and calcium nitrate dissolve starch at ordinary temperatures Even in small quantities they accelerate gelatinisation, and are used for this purpose in the preparation of adhesives. Thiocyanates and, in particular, calcium thiocyanate are particularly active, causing gelatinisation or solution at ordinary temperatures, according to the concentration

All salts which are hydrolysed in water promote gelatinisation. Alum and magnesium chloride, which give acids when hydrolysed, are used in the preparation of both adhesives and dressings. Acid salts, such as sodium bifluoride or sodium hydrogen sulphate, act still more energetically. Pastes produced in this manner tend to coagulate on keeping or to become "thin" when heated.

Salts which, when dissociated, give alkaline solutions, such as borax or sodium phosphate, act, of course, like weak solutions of caustic alkalis

Neutral salts which are not hydrolysed by water have, as a rule, little gelatinising action, but, in many cases, they precipitate starch from its solutions, or inhibit its gelatinisation If a solution of starch be saturated with sodium sulphate the starch is completely precipitated. If a solution of sodium hydroxide be saturated with sodium sulphate and mixed with starch, the latter does not become gelatinised, although the granules are ruptured. If the starch be filtered off, dried at a low temperature, and neutralised by means of powdered oxalic acid or an alcoholic solution of any other acid, the dry product gelatinises completely when mixed with cold water "Cold water" starch powders are made in this way It was mentioned above that a similar effect can be obtained by the prolonged grinding of starch with sand The action of all bodies which promote gelatinisation appears to be that of rupturing the starch granules A few examples of these preparations may be given. In Fr Pat 365834, 1906, the starch is stirred into a concentrated solution of sodium sulphate and sodium hydroxide is then added. The alkali is neutralised by an acid or a salt of ammonium or magnesium and the product dried at a low temperature Or alcoholic sodium hydroxide is used (Eng Pat 5574, 1904), or organic liquids, such as paraffin or carbon tetrachloride In a more recent patent process (*J.S C I*, 1922, 724A) the starch is treated with concentrated alkali hydroxide below 0° C so that no paste is formed, and the quantity of alkali hydroxide is so regulated that, on allowing the temperature to rise, the reaction which takes place causes the disruption of the starch granules without gelatinisation It is not necessary to suspend the starch in water-repelling liquids before treating it with the alkali hydroxide The product can be used with advantage in the textile industry for finishing, as a thickening agent in calico printing, as a size, or for wall-papering The Arabol Co use the following process. One hundred parts of dry farina are mixed with 80 parts of a 50 per cent. solution of ammonium thiocyanate to which 40 parts of alcohol have been added, and a little sodium sulphite to prevent iron discoloration The starch is then washed with alcohol or acetone till free from thiocyanate

The Action of Formaldehyde.—If starch be allowed to stand for some days in contact with formalin, an opalescent liquid is produced from which the starch can be precipitated unchanged by means of alcohol. A similar result is produced by digesting starch with small quantities of formaldehyde at a higher temperature. The formaldehyde does not combine with the starch, but appears to act as a catalytic agent. The solution of starch in formaldehyde does not

give the characteristic blue colour with iodine, though it regains this power when ammonium acetate is added to the solution. But if starch be heated with formaldehyde at a low temperature below its point of gelatinisation and then dried, the resulting product, although it swells up when mixed with water, cannot be gelatinised This action is more complete when an ammonium salt is added in the proportions necessary to form hexamethylenetetramine, *e g* 5 to 10 per cent of formaldehyde and 6 to 11 per cent. of ammonium chloride.

The Action of Acids.—The first action of acids upon starch is to change it into soluble starch and then into dextrin. Prolonged action of the acid then causes hydrolysis to take place, resulting in the formation of glucose. Thus, simplification of the molecule takes place, producing a substance with progressively less marked colloidal properties, and becoming more soluble and diffusible. This is followed by hydrolysis to non-colloidal readily diffusible glucose—

$$\underset{\text{starch}}{(C_6H_{10}O_5)_n} \rightarrow \underset{\text{soluble starch}}{(C_6H_{10}O_5)_{n'}} \rightarrow \underset{\text{dextrin}}{(C_6H_{10}O_5)_{n''}}$$

$$(C_6H_{10}O_5)_{n''} + n''H_2O = n''\underset{\text{glucose}}{(C_6H_{12}O_6)}$$

The rate at which these changes take place depends upon the hydrogen-ion concentration of the acid used, the quantity present, and the temperature of the reaction Thus, cold concentrated hydrochloric acid dissolves starch, immediately forming a clear jelly If this be diluted with water quickly and treated with excess of alcohol, soluble starch is precipitated If the mixture be allowed to stand for a short time before adding alcohol, the precipitate will be found to contain dextrin, which increases gradually in quantity while the starch decreases But, at the same time, the dextrin undergoes hydrolysis, and finally only glucose is present Pure dextrin may be made by dissolving starch in moderately concentrated sulphuric acid, neutralising the acid quickly with alkali and adding excess of alcohol The different products of the reaction may be separated by using suitable concentrations of acid and controlling the temperature Thus, when starch is mixed with a cold 10 per cent solution of hydrochloric acid and allowed to stand for some days it is converted almost quantitatively into soluble starch, which can be separated by filtration and purified by repeated washing with water Still more dilute acid (*e g* 1 per cent) will bring about the same change at the boiling-point, but, in this case, the starch is dissolved and must be precipitated, after careful neutralisation of the acid, by means of alcohol At temperatures above the boiling-point, so small a concentration of acid as 0·05 per cent is sufficient to convert starch into soluble starch But, in all cases where the mixture is heated, dextrin and glucose are also produced—that is, all the reactions proceed simultaneously.

When starch is boiled for some hours with a dilute acid glucose is the chief product, but some unchanged dextrin may be present as in commercial starch syrup If starch be treated with small quantities of acid, dried, and heated to a temperature of about 200° C , it is converted chiefly into dextrin, together with small proportions of soluble starch and glucose. Soluble starches, dextrins, and " thin " starches are made in this way.

The nature of the end-products as well as the velocity of inversion is dependent to a great extent upon the hydrogen-ion concentration of the acid used. Hydrochloric and sulphuric acids act rapidly. Similarly, among organic acids, chloracetic and the sulphonic acids change starch rapidly into soluble

starch and dextrin at the boiling-point. But most of the organic acids, owing to their low hydrogen-ion concentration, are comparatively inactive.

Nitric acid acts in the same way as with cotton, giving nitro compounds, and if the time of action be prolonged or the mixture heated the starch is completely broken down, oxalic acid and other oxidation products being formed.

Organic acids, such as acetic acid, also give rise to esters, as they do with cellulose. Thus, acetic anhydride produces acetate of starch which is known commercially as "feculose"

Feculose is of some importance It differs little in appearance from ordinary starch, and when boiled with water gives a clear homogeneous solution which does not set on cooling. It gives the usual blue colour with iodine, does not reduce Fehling solution, and is precipitated from its solutions by alcohol and such salts as sodium or magnesium sulphate It is used in confectionery and paper manufacture, and also for textile dressings Traquair (*J S C I*, 1909, p 291) says that since it is a true colloid it gives lustre, substance, and "handle" to cotton goods, while the clear film which it forms makes it specially useful for bright coloured goods. On light cottons where no softener is used, 1 lb of feculose per gallon is equal to from 3 to 4 of dextrin When used with ordinary starch it confers flexibility and clearness on the finish, leaving the proportion of starch to be varied according to the degree of stiffness required

The Action of Micro-organisms and Enzymes.— Starch, unless perfectly dry, is attacked readily by moulds, bacteria, and yeasts The products of this action vary with the micro-organism, but they include commonly such bodies as organic acids, soluble starch, dextrin, and sugar Many organisms produce coloured growths Thus, *B mesentericus* gives rise to a red colour when grown on starch paste, while moulds, black and pink *Torulæ*, are also chromogenic Badly kept starches are often acid in reaction, owing to decomposition by acid-forming organisms, and consequently become "thin" when boiled The complete destruction of a starch dressing may result also from similar causes. Antiseptics, such as zinc chloride, are commonly included in starch dressings and sizes to inhibit the growth of micro-organisms These will be described later. Certain organisms, such as *B macerans* and *B subtilis*, are said to change starch completely into dextrin When micro-organisms decompose starch they do so because they secrete an enzyme which acts as a catalytic agent (see Chapter X) Thus, bacterial action is really enzymitic in nature

There are, however, many enzymes not associated with micro-organisms, which are able to decompose starch These include amylase, which is present in the saliva and pancreatic juice of animals, and diastase, which occurs in germinating grain and other vegetable tissues, and also is secreted by micro-organisms. The action of diastase on starch is very important in bleaching. It is prepared by extracting green or air-dried malt with dilute spirit, filtering, and adding an excess of alcohol to the filtrate The precipitate which is formed contains the diastase, together with other bodies It is redissolved in dilute spirit, the solution filtered and again treated with alcohol The crude enzyme is filtered off, dissolved in water and dialysed Enzymes, being colloids, are thus separated from the accompanying diffusible impurities After dialysis the diastase is again thrown down by alcohol, filtered off, and dried at a low temperature It is a white amorphous powder, soluble in water, of which a very small quantity can liquefy a very large amount of starch

In textile processes malt extract is generally used instead of diastase This is made by extracting green malt with cold water and filtering the mixture. The filtrate is evaporated to a thick syrup at a low temperature and under

reduced pressure. The extract contains all the diastase of the original malt. Diastase has no action on ungelatinised starch in the cold but dissolves it if previously gelatinised, or if the starch granules are ruptured by any other means. But when starch is mixed with water and digested with diastase at a temperature of from 65° to 70° C, the reaction of the mixture being either neutral or faintly acid, it is changed rapidly into soluble starch and then into a mixture of maltose and dextrin. These changes take place simultaneously, and the relative proportions of the two final products depend upon the conditions of the reaction. The action of the enzyme becomes restricted at temperatures between 65° and 70° C, and at about 80° C is permanently destroyed, *i e* on cooling the mixture it does not again become active. Its activity is destroyed also by even traces of alkali

According to O'Sullivan, the change takes place in accordance with one of three general equations, with sufficient time for completion At temperatures up to 60° C the chief product is maltose, in accordance with the equation

$$(1)\quad 6C_{12}H_{20}O_{10}+4H_2O=\underset{\text{maltose}}{4C_{12}H_{22}O_{11}}+\underset{\text{dextrin}}{2C_{12}H_{20}O_{10}}.$$

At 66° C the proportion of dextrin is increased, as shown by the equation

$$(2)\quad 6C_{12}H_{20}O_{10}+2H_2O=2C_{12}H_{22}O_{11}+4C_{12}H_{20}O_{10}.$$

At a temperature of 70° C a still greater proportion of dextrin is obtained—

$$(3)\quad 6C_{12}H_{20}O_{10}+H_2O=C_{12}H_{22}O_{11}+5C_{12}H_{20}O_{10}$$

If malt extract be heated to 67° C for a few minutes and then cooled to 60° C. its action upon gelatinised starch is that of equation (2) and not (1) Similarly, if heated to 75° C and then added to starch at 68° C the products are those of equation (3) These points are of special interest in the production of thin starches and dextrins by means of diastase

Diastatic ferments can be prepared also from cultures of many micro-organisms Thus, "taka diastase" is obtained from *Aspergillus oryzæ*. It is extremely active, converting starch into a mixture of maltose and dextrose at a temperature of 38° C *Aspergillus niger* produces a similar enzyme, while those of *B subtilis* and *B. macerans*, as mentioned above, give chiefly dextrin and very little maltose

Animal amylases are contained in the saliva and pancreatic juice The latter acts best in a faintly alkaline solution and is, unlike diastase, destroyed by acids

These starch-dissolving ferments are made use of for clearing goods from starch before bleaching (Chapter XV.) Another important application is the preparation of dressings containing soluble starch and dextrin. "Diastafor," a well-known preparation, may be used for this purpose. The general method of preparation is as follows .—

For each 25 lbs of potato starch from 4 to 8 ozs. of diastafor are dissolved in lukewarm water. The starch is mixed with water and the mixture heated to a temperature of 150° to 160° F. The diastafor is then added and the mixture kept well stirred at a temperature not exceeding 160° F. until the desired consistency is obtained. This usually takes from five to fifteen minutes The action of the enzyme is then stopped immediately, either by raising the temperature quickly to the boiling-point or by adding sufficient alkali to give the mixture an alkaline reaction to litmus paper. When starches other than potato are used, with comparatively high gelatinising points, they must be gelatinised

and the mixture then cooled to from 150° to 160° F before adding the diastafor. The following examples of dressings are given by Messrs R W Greef & Co —

1 **Dressings for Cotton Warps.**—(1) Take 10 lbs potato starch, 10 gallons water, 2½ ozs diastafor Stir the starch with a little cold water, make into a paste with boiling water and cool to 160° F Add the diastafor dissolved in a little lukewarm water, and stir for ten to fifteen minutes until clear and liquid Boil up

The dressing is to be used warm, and may be conveniently made in a vessel provided with a mechanical stirrer and connected with the dressing machine by a pipe

(2) 25 lbs potato starch are sifted into 30 gallons boiling water and 1 lb glue, previously soaked overnight, added Thoroughly stir and add 2 lbs tallow (for heavy warps also 2 lbs Japan wax), and boil up with constant stirring When thoroughly mixed, cool to 160° F, add 5 ozs diastafor, stir for ten minutes and again boil

2 **Dressing for Skeins.**—To 15 gallons of boiling water add 6 lbs size or 2 lbs gelatin Whilst boiling add 25 lbs potato starch suspended in 10 gallons water Boil for a short time and cool whilst stirring to 160° F Then add 4 ozs diastafor dissolved in 1 quart lukewarm water Stir well for ten minutes and boil up If to the hot mass 2 lbs melted beeswax be added gradually and well stirred in it increases the gloss and suppleness of the skeins

3 **Thick Dressings** Dissolve 2 lbs diastafor in 25 gallons water at 104 F Add 60 lbs starch Raise the temperature to 160° F and stir until all the starch has dissolved to a milky mass Boil and allow to cool When cold add 55 lbs starch, stirring well, and raise to 212° F As soon as the mass has become pasty and even, cool to 160° F again, add 2 lbs diastafor, stir well until clear and boil up

4 **Malto-dextrine Stock for Finishes.** To make 40 gallons, make into a paste 200 lbs potato starch and 24 gallons cold water Add 3½ lbs diastafor dissolved in 1 gallon water at 100° F Thoroughly stir, raising the temperature to 160° F until the mass becomes thin in about ten to fifteen minutes, then raise to 212° F and make up to 40 gallons

5 **Calico Finish.**—To 40 gallons malto dextrine stock add 2½ gallons softening oil, ½ gallon crude glycerin and 15 lbs Glauber salt (not for blacks)

When making dressings with diastase it is important not to prolong the treatment, since this increases the proportion of dextrose This body not only has no stiffening power, but on the contrary is hygroscopic, and gives goods a damp feel It is liable also to become converted into caramel and thus cause discolorations

The difficulty connected with the use of diastase in preparing dressing mixtures is to control the quantity of sugar produced Animal amylases give much less sugar and consequently a higher proportion of soluble starch or dextrin Thus, diastrol DS and DB, also known as fermasol DS and DB, have a high liquefying power towards starch and produce very little sugar One part of the preparation liquefies from 25,000 to 30,000 parts of starch, producing no colour According to Taghani (*J Soc Dyers and Col*, 1921, p 306) the addition of from 0 5 to 2 5 grammes of salt per litre assists the action A more recent preparation containing amylases is "rapidase," which can be used at comparatively high temperatures and in the presence of an alkali such as sodium carbonate It is suitable both for removing starch from cotton goods and for making dressing mixtures of soluble starch and dextrin Three examples may be given

1. For a soft finish containing 1 in 6 of soluble starch. A vat is prepared with 30 gallons of water heated to 194° F. In another vat above this 100 lbs. of starch are mixed with 20 gallons of cold water and 2 lbs of rapidase After mixing well, the cream is run slowly into the lower vat, the temperature being kept at 194° F for half an hour. The mixture is then heated to the boiling-point for from ten to fifteen minutes to stop the diastatic action.

2 Stiff finish containing 1 in 4 of starch. The vat is prepared with 15 gallons of water heated to 193° F. In the mixing vat are placed 150 lbs. of starch, 30 gallons of cold water, and 1·5 lbs of rapidase. This is run slowly into the lower vat, the temperature of which is kept at 194° F for half an hour and then raised to the boiling-point as before.

3. If a very soft finish containing a large proportion of dextrin be required, the mixing is carried out at 176° to 185° F. After half an hour the mixture is allowed to cool off for an hour or two It is tested periodically with iodine solution and, when no starch coloration is produced, raised to the boiling-point for a few minutes These reactions can only be brought about if the mixture is neutral or slightly alkaline Acid inhibits the action

Action of Oxidising Agents.—Oxidising agents when used in comparatively small quantities convert starch into soluble starch Hypochlorites, chlorates, chlorine, permanganates, bichromates, persulphates, perborates, and sodium peroxide are all used for this purpose, with or without the assistance of an oxygen carrier For example

1. 1500 kg of farina are mixed with 1000 litres of water and 300 to 400 kg of a solution of sodium hypochlorite of 1·285 sp gr and allowed to stand for some hours The starch is then filtered off, washed with water, pressed, and dried

2 Eng Pat 179765, 1921 100 kg of flour are mixed with 2·5 kg of ammonium persulphate and 1 kg of ammonia solution (22° Bé) and allowed to stand for not less than twenty-four hours

3 25 kg of starch are treated at ordinary temperatures with 50 litres of a solution containing 2 to 4 grammes of potassium bichromate and 150 grammes of sulphuric acid per litre. After some hours the starch is filtered off, washed with water, and dried at 30° C.

Name	Outline.	Measurement	Surface	Hilum.	Markings
Potato	Oval or elliptical .	mm. 1/25 long diam 1/37 short „	Uniformly but slightly convex	Dark spot near the narrow end	Concentric rings closed or almost closed curves
Rice . .	Rectilinear and polygonal	1/250 . .	Flat .	None . .	None
Maize .	Rectilinear and polygonal.	1/70 . . .	Uneven and slightly concave	Stellate or irregular large central	None.
Wheat .	Circular or nearly so.	1/50 . . .	Convex . .	Dark spot eccentric.	Occasionally a few exceedingly faint concentric rings
Arrowroot (Bermuda)	Oval . .	1/28 long diam 1/45 short „	Uniformly but slightly convex	Nearer broad end circular crucial transverse line or slit	Faint concentric rings in a few cases extending about ⅓ length of grain.
Cassava .	Rectilinear and polygonal	1/70 . . .	Uneven and slightly concave	Stellate or irregular large central.	None.

The Identification of Starch.—Starch is detected by the fact that it forms a deep blue-coloured compound or solution when treated with a solution of iodine

in potassium iodide If this reagent be added to starch powder the latter becomes almost black in colour If the starch be gelatinised and dissolved a deep blue colour is produced, or if excess of iodine be added, a blue precipitate If a suspension of starch in water be treated with iodine solution under the microscope, the deeply blue-coloured grains can be recognised easily The origin of a starch can be determined only by means of a microscopic examination and comparison with known samples But this can only be done when the starch grains are intact When they have been gelatinised they have no longer their characteristic differences The table on p. 579 gives the characteristics of the more important starches, and fig 194 illustrates the microscopic appearance of the granules

The Estimation of one, two, or more different Starches in Mixture. —This can only be done approximately. Several slides are made and examined

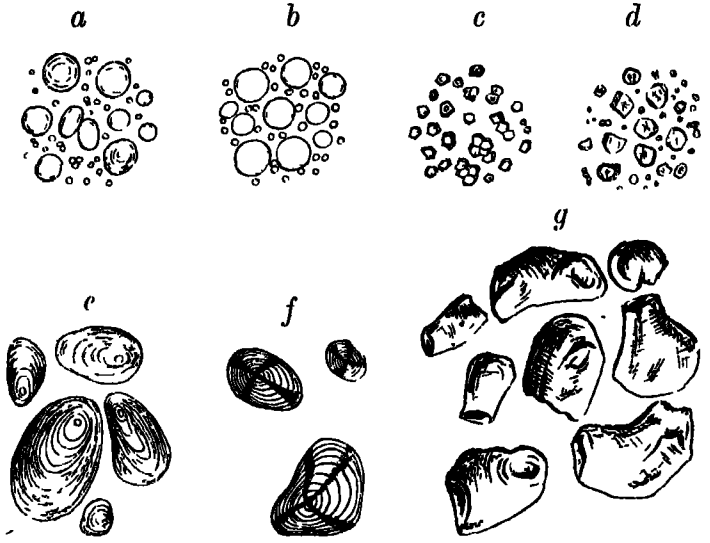


FIG 194 —Starch granules from (*a*) barley, (*b*) wheat; (*c*) rice, (*d*) maize, (*e*) potato, (*f*) potato, in polarised light, ×300 (*after Stirling*), (*g*) sago (*after Davies*)

under the microscope The number of typical granules of each kind is counted in several different fields of view Trial mixtures of the two, containing known percentages of the starches, are made up and examined in the same way The results of the count are then compared with those of the sample. The following details are given in Allen's *Commercial Organic Analysis*, vol i p 412, for ascertaining the proportions of barley or wheat in oatmeal —

"Genuine pearl-barley is ground finely in a mortar, and a series of standards made by mixing the flour with definite proportions of genuine oatmeal Mixtures containing 5, 10, 15, 20, 30, and 40 per cent of barley respectively will be found convenient in practice The sample of oatmeal is thoroughly mixed, and 0·1 gramme weighed out and ground in an agate mortar with a little water When the mixture is perfectly smooth it is rinsed into a small conical glass and diluted with water to 10 c c. Two of the standard mixtures (say the 10 and 20 per cent mixtures) are then treated in a precisely similar manner A drop of the sample and one of each of the standards are then placed on glass slides and

covered with thin covers. Care must be taken that the starches and water are thoroughly agitated, so that the drops taken shall be representative, and it is important that the drops themselves shall be of exactly the same size. These conditions are best ensured by immersing in the liquid a short piece of glass tube drawn out to a fine point, blowing down it so as to mix the sample thoroughly by means of the air-bubbles expelled, and then allowing a drop of the liquid to fall from the orifice on to the glass slide The same tube is then employed to take drops of the standard mixtures. The cover glasses must all be of equal size, and sufficiently large to take up the whole of the drop, as none of the liquid must be removed. The slides having been prepared, the number of barley granules visible in twelve successive fields is noted. The standards are then similarly observed, the operation being repeated until a standard mixture is found, the barley granules in twelve fields of which are equal, or nearly equal, to those counted in the sample The proportion of wheat or barley in the sample will then be approximately the same as that in the standard it agrees with "

Commercial Starches.—The most important are wheat, potato, and maize starches. Potato starch is generally known as farina , maize starch being termed simply " starch " or corn starch. Sago, tapioca, and cassava starches are used chiefly in sizing, rice starch, though employed largely in laundry work, finds little application in finishing Wheat starch gives a somewhat thin paste with considerable penetrating power. It enters into intimate association with the cloth, imparting to it a feeling of increased thickness, leaving the surface with a smooth feel and brightened appearance The latter qualities are developed considerably by the operations of beetling and calendering, and in this way a high degree of glaze can be produced The binding properties of wheat starch are also well marked Maize starch possesses properties very similar to those of wheat starch, but gives a thicker paste which requires more boiling It imparts a firm feel to the goods It is also a binding agent, and is capable of taking a high degree of glaze Cassava, though a root starch, is very similar to maize, which it is to some extent replacing Farina or potato starch produces a thick paste, which for thick " makings " is of importance. It gives cloth a thick, smooth feel, with dull or rough surface effects Its capacity for holding filling materials is some 20 per cent less than that of maize starch, but the properties of different starches can be blended, and by using mixtures in suitable proportions a desired result may be obtained A dress of potato starch is rather liable to turn off on keeping.

Tapioca starch gives a medium thick paste which penetrates well but has less binding power than either wheat, maize, or farina. It gives a transparent film when dried, with a soft feel It is useful for light goods or those with bright coloured borders. Sago starch or flour gives a thin but very adhesive paste, which will stand a considerable amount of boiling without losing its strength It penetrates well, and imparts considerable tensile strength to yarns. It is used chiefly for sizing Examples of the use of the different starches are given under " Processes " (Chapter XXVII)

A good sample of starch should not contain much more than 10 per cent. of water Damp starches are often mouldy or sour. When mixed with distilled water, the reaction of starch should be neutral or very faintly alkaline Acidity may be due to fermentation, but, also, to the presence of acid used in the manufacture, or a bleaching agent such as sulphurous acid If a cold aqueous extract of a starch decolorises centinormal iodine solution it may contain free sulphurous acid. Sometimes a starch, which appears to be of a good colour in mass, will show unevenness when spread out in a thin layer. This may be due to overheating in drying or to the presence of impurities. Starches made by the

fermentation process are often of poor colour. The white colour should not change when the starch is moistened with dilute acid or sodium carbonate, nor should it give any colour to water or spirit. Any changes observed would indicate the presence of blueing agents for the purpose of improving a naturally poor colour Well-prepared starches should be practically free from nitrogen, or, at any rate, contain only traces (*e g.* 0 1 per cent). Wheat starches and others, if made by fermentation processes, contain sometimes distinct quantities of nitrogenous compounds. These indicate incomplete removal of the original impurities. Such starches rarely keep well, since the nitrogenous constituents serve as good food material for moulds and putrefactive organisms. The percentage of ash in starch is very small, and it contains only traces of matter soluble in cold water

The following table illustrates these points —

	1.	2	3
Water .	10 50	13 00	19 50
Ash .	0 25	0 05	0 20
Soluble matter	0 50	0 25	traces
Starch . . .	88 75	86 70	80 30
Acidity calculated as sulphuric acid	0 07	0 00	0 00

Sample No 1 gave a blue ash, indicating the presence of smalt It contained also 0·23 per cent. of nitrogen The goods dressed with it had developed mould on storing Sample No 2 is a good one, while No 3 contains an excess of moisture

The Analysis of Commercial Starches.—*Moisture*—Five grammes are dried in a flat dish at 100° to 105° C. till no further loss of weight occurs

Mineral Matter of Ash.—This is determined by igniting about 5 grammes in a platinum dish till it is completely burnt

Matter Soluble in Water—Five grammes of the starch are ground into a cream with a little distilled water and washed into a 250 c c flask and made up to the mark with cold distilled water The flask is allowed to stand, with occasional shaking, for about six hours. The contents are then filtered. The soluble matter in the filtrate is determined by evaporating a measured volume to dryness on the water-bath and weighing the dried residue. Good starches contain practically no soluble matter Another portion of the filtrate is tested for acid or alkali and the quantity titrated if present The appearance of the soluble residue should be noted after drying If it is brown or black the starch is likely to lose its colour on storing, and should be regarded with suspicion.

Starch—The sum of the moisture, ash, and soluble matter deducted from 100 gives approximately the percentage of starch present

When a direct determination is required one of the following methods may be used .—

1 Two grammes of the sample are boiled with 2 per cent sulphuric acid under an inverted condenser till the solution no longer gives a blue colour with iodine About six hours' boiling is generally necessary The liquid is then cooled, made faintly alkaline with sodium hydroxide, and diluted to a known volume. The dextrose produced by hydrolysis is estimated by means of Fehling

solution in the manner described already, and its equivalent of starch calculated. Or the weight of cuprous oxide multiplied by 0·4171 gives starch directly.

2 *Von Fellenberg's Method* (*J.S.C.I.*, 1917, p 935).—From 0·3 to 1 gramme of finely ground fat-free material is moistened with water and mixed with 20 c.c. of 50 per cent. calcium-chloride solution. The mixture is heated in boiling water for thirty minutes to dissolve the starch It is then cooled, made up to 100 c c , and filtered or centrifugalised. Fifty c c. of the filtrate are treated with N/50 iodine solution till a flocculent precipitate is obtained, but avoiding a large excess of the reagent After standing twenty-four hours a little asbestos pulp is added, and the mixture is filtered through an asbestos mat on a Gooch crucible. The precipitate is washed four times with 50 per cent calcium-chloride solution containing a little iodine, and then with 60, 85, and 95 per cent. alcohol successively The crucible is then dried and weighed It is then ignited and weighed again The difference between the two weights gives the amount of starch present.

3 *Polarimetric Determination of Starch* —In Lintner's method (*J.S.C.I.*, 1907, p 281) 5 grammes of the starch are ground to a smooth paste in a mortar with 20 c c of water, 40 c c of hydrochloric acid (sp gr 1·19) are then added, and the mixture allowed to stand for thirty minutes to dissolve the starch. It is then washed into a 200 c c flask with hydrochloric acid of 1·125 sp. gr. Proteins, if present, are precipitated by adding 10 c.c. of a 4 per cent. solution of phosphotungstic acid The mixture is then made up to 200 c c. with the diluted hydrochloric acid, shaken, and filtered. The rotation of the filtrate is measured in a 200 mm tube

The starch is calculated from the formula $a_D = 200 \cdot 3$ for barley starch

Ewers (*Analyst*, 1908, p. 101) uses a somewhat different polarimetric method of estimation, which he carries out as follows —

" Place 25 c.c of glacial acetic acid in a 200 c c flask without wetting the neck. Introduce 10 grammes of the substance, close the flask, and shake vigorously till the mixture is uniform Wash down the stopper and neck of the flask with 25 c c of glacial acetic acid. Heat the flask in boiling water for ten minutes Then add 10 c c of dilute hydrochloric acid (10 c c. of the 25 per cent acid per 100 c c) and heat in the water-bath for exactly six minutes, shaking round every minute Add hot water to 180 c.c and leave for a further ten minutes in boiling water Cool to 20° C and add 2 to 3 c.c. of saturated potassium-ferrocyanide solution, dilute to 200 c c., filter and polarise. If the filtrate be not clear use a little zinc sulphate A blank experiment is then carried out as follows . Five grammes of the substance are placed in a 100 c c flask with 70 c c of water at 50° C (for potato, 35° C.) and mixed by shaking. Digest at 48° to 50° C. for half an hour (potato at ordinary temperatures). Add 25 c c of glacial acetic acid and continue digestion at the same temperature for half an hour (potato, fifteen minutes) Then bring temperature to 20° C , add ferrocyanide as before, dilute to 100 c.c , filter and polarise The specific rotatory power of starch at 20° C at 5 per cent. concentration under these conditions is "—

Wheat starch	+183 62
Rice starch	+186 07
Maize starch	+184 19
Potato starch	+186 46

A simpler process is that of Wenglein (*J S C I* , 1908, p. 238). Five grammes of the sample are made into a uniform paste with 20 c c of water in a mortar and 40 c.c. of sulphuric acid (sp gr 1·70) are stirred in. The liquefied mixture is transferred to a 200 c.c. flask after standing for fifteen minutes. The mortar

is washed out with sulphuric acid (sp. gr. 1·30) Ten c.c of a 4 per cent. solution of phosphotungstic acid are then added and the contents of the flask are made up to the mark with water, mixed, and filtered. When the filtrate comes through clear it is collected and polarised The factor $a_D=191·7$ is used for calculating the starch

Thorne and Jeffers' modification of Lintner's process (*Analyst*, 1909, p 332) is recommended by Baker, and the method is described in the *Reports to the Local Government Board* on public health and medical subjects (New Series, No. 80). For the estimation of starch, 5 grammes of the substance are ground in a mortar with 10 to 15 c c of water, followed by 15 to 20 c c of hydrochloric acid of sp. gr 1·15 added in quantities of 5 c c at a time The starch quickly forms a viscous mass, which in the course of a few minutes becomes thin After standing half an hour, the mixture is transferred to a 200 c c flask containing 10 c c. of a 4 per cent solution of phosphotungstic acid and 20 c c of hydrochloric acid of sp gr 1 15 The mortar is washed out with hydrochloric acid of 1·1 sp gr and the contents of the flask made up to the mark with acid of the same strength After being well shaken and again allowed to stand for at least half an hour, the liquid is filtered and polarised in a 200 mm tube at 20° C., with a Schmidt and Haensch scale and a white light The percentage of starch (P) is calculated from the reading (R) by the formula

$$P=\frac{R\times 40}{11·6}$$

This formula involves the assumption that soluble starch has a specific rotatory power of + 200, a value probably somewhat too high.

4 *Taka diastase* converts starch completely into maltose and dextrose at a temperature of 38° C This reaction may be made use of for the determination of starch (Revis and Burnett, *Analyst*, 1915, p. 429) Five grammes of the substance are stirred with 50 c c of 10 per cent alcohol (by volume) and filtered under pressure The residue is washed twice with 50 c c of 10 per cent alcohol, and finally with 10 c c of 95 per cent alcohol The starch is transferred to a 250 c c flask with about 125 c c of boiling water and well mixed. The flask is then placed in boiling water with constant shaking for fifteen minutes to gelatinise the starch. After cooling to 38° C, 0·05 gramme of taka diastase, rubbed up with a little water, and 2 c c of toluene are added. The flask is shaken, closed, and kept at 38° C for from twenty-four to thirty-six hours, shaking at intervals The action of the diastase is inhibited by adding 10 c.c. of N/10 sodium hydroxide The flask is cooled to 15° C and about 100 c c of water are added, and then 10 c c of acid mercuric nitrate solution run in on the surface, followed by sufficient water to bring the volume of the liquid to the mark below the toluene. The contents of the flask are then mixed and filtered. To 100 c c of the filtrate, which should be perfectly bright and colourless, carefully measured into a flask, is added 0·5 gramme of sodium phosphate, $Na_2HPO_4.12H_2O$, and after this has dissolved, 10 c.c. of sodium-hydroxide solution with agitation The contents of the flask are mixed and filtered, and the gravimetric copper reduction and polarimetric reading of the filtrate are determined The mercuric nitrate solution is made by dissolving mercuric oxide in twice its weight of nitric acid (sp. gr. 1·42) and diluting with five times its volume of water.

A simpler method of using taka diastase is that of Davis (*J.S C.I.*, 1916, p. 207). The starch is first extracted with 80 per cent alcohol to dissolve sugar, and then with cold water to remove gum. Two grammes are then heated with

200 c.c. of water till completely gelatinised. The mixture is then cooled to 38° C, 0·1 gramme of taka diastase and 2 c c of toluene are added, after which the mixture is digested at 38° C for twenty-four hours. It is then heated to 100° C and filtered into a 500 c c flask and the filter washed until the filtrate measures 475 c c Lead acetate is added, and the volume is made up to 500 c c and filtered The lead is precipitated in 100 c c of the filtrate with sodium carbonate, after which the volume is made up to 110 c.c The liquid is then filtered and the sugar estimated as above

Determination of the Viscosity of a Starch Solution.– Ermen's method of testing starches has been mentioned on p 573 Archbutt's viscometer is described under Glue For starch solutions, the falling sphere process of Gibson and Jacobs is more suitable (*J S C I*, 1920, 558A)

A tube 29 cm long and 2 cm internal diameter is arranged vertically in a bath provided with a stirrer and thermometer The tube is divided into three 5 cm lengths for measurement of the time of fall, and a further 5 cm above for the sphere to acquire uniform velocity The sphere is a steel ball, 0·15 cm diameter, as used for ball-bearings, and it is introduced into the viscometer tube by means of a short length of glass tubing, 3 mm diameter, fixed by means of a rubber stopper and adjusted to dip 3 cm below the surface of the liquid The following equation gives the viscosity —

$$9\eta S(1+2{\cdot}4x)(1+3{\cdot}3r/h)=2gr^2(s-\sigma)T,$$

where T is the time of fall through a length, S, r is the radius and s the density of the sphere, σ the density of the liquid, x the ratio of the radius of the sphere to that of the viscometer tube, and h the height of the liquid. This equation reduces itself to $\eta=K(s-\sigma)T$, where K is the numerical constant involving all the corrections for the particular tube This constant having been found, either by the use of the first equation above or by experiment with a liquid of known viscosity, determinations for other substances simply resolve themselves into determinations of s, σ, and T For castor oil at 20° C the value $\eta=9{\cdot}888$ was found by this method, a figure in close agreement with Kahlbaum and Raber's value

Soluble Starch $(C_6H_{10}O_5)_n$ —This modification of starch is the first product of the hydrolysis of ordinary starch, and it has the same percentage composition, but it is probable that it has a smaller molecule, or forms smaller molecular aggregates

The methods by which soluble starch can be obtained have been indicated already, but they may be summarised briefly. They are—

1. By heating starch for a long time at a temperature below that required to convert it into dextrin
2. By heating starch with water under pressure
3. By heating starch with small quantities of acids
4. By treating starch with cold moderately dilute mineral acid, *e g* 10 per cent. hydrochloric acid
5. By treating starch with a cold solution of an oxidising agent.
6. By treating starch with alkalis
7. By treating starch with enzymes

Soluble starch is prepared best by method (4) With nearly all the others both dextrin and dextrose are also produced.

The powdered starch is soaked for some days, with occasional stirring, in a

cold 10 per cent. solution of hydrochloric or sulphuric acid till a sample, when washed and dissolved in hot water, does not set to a jelly on cooling. The acid is then drawn off and the starch is washed with water till free from acid. Sedimentation may be made use of, the starch being mixed with a considerable volume of water and then allowed to settle. Soluble starch may be made also by mixing starch with a dilute solution of an acid, *e g.* a 0·01 per cent. solution of hydrochloric acid, drying and heating the dry product for some time at a low temperature. A certain amount of dextrin and even dextrose is produced at the same time.

As an example of another method Kantorowitz's patent process (Eng Pat 5844, 1896) may be mentioned Starch is gelatinised by a solution of sodium hydroxide The alkali is then carefully neutralised by a dilute acid and the neutralised solution is treated with magnesium sulphate to precipitate the starch. The precipitated starch is filtered off, pressed, and dried at a low temperature. Or, as mentioned above, if the starch be mixed with a strong solution of sodium sulphate before adding the alkali, swelling is prevented and precipitation unnecessary.

Soluble starch is a white powdery substance with the same appearance as that of ordinary starch If made by a cold process it retains its granular structure, and is not easy to distinguish from ordinary starch by microscopic examination, except that some of the granules are always ruptured or the hilum fractured. When it is made by heating starch with chemical reagents, it loses its characteristic form and appears to be structureless Ordinary soluble starch (except cold-water starch) does not swell nor dissolve in cold water, but dissolves readily in boiling water, forming a perfectly clear solution with a low viscosity compared with that of a similar solution of the original starch When this solution is cooled it does not set to a paste or jelly like ordinary starch, unless unchanged starch be also present. Thus, while a 10 per cent solution of ordinary starch gives a stiff paste, a solution of soluble starch of the same concentration remains liquid when cooled But if the solution be allowed to stand for some time insoluble starch is gradually precipitated Soluble starch (*Report on Colloidal Chemistry*, vol i p 51) usually contains a higher mineral content than ordinary starch, namely, about 1·5 per cent, and if this be alkaline it must have some effect on the properties. The amount of water is also higher (17 to 21 per cent), and when heated with caustic alkali it yields a higher percentage of acetic acid, equivalent to about 13 per cent of potassium hydroxide, pointing to a molecular change having taken place

Soluble starch, owing to its solubility and the low viscosity of its solutions, penetrates cotton readily, and when dried it gives a continuous transparent film and not a discontinuous one like ordinary starch paste It gives cloth a fuller feel than ordinary starch, but has little binding power for filling agents. It is therefore chiefly useful for finishes where a full feel is required without mineral filling. It is used under the name of *thin starch* This is, however, not soluble starch, but variable mixtures of soluble starch with unchanged starch, dextrin, and dextrose It is made, commonly, by moistening starch with very dilute nitric acid and drying it at a low temperature It was explained above that it is very difficult to use these processes without producing both dextrin and dextrose. Moreover, thin starches are nearly all acid When they are boiled they become thin quickly, partly owing to the hydrolysing action of this residual acid.

The following table shows the composition of some commercial "thin" starches —

	1.	2.
Water	8 00	10·40
Mineral matter	0 05	0·00
Dextrin	22 86	20 25
Dextrose	7 03	6 95
Starch	62·06	62 40
Acidity	0 07	0·35

Starches containing such large quantities of dextrose readily become sour, since this body favours the growth of aerial yeasts and acid ferments They are also liable to discolour goods on keeping or drying owing to the formation of traces of caramel This tendency is greatly augmented by the presence of free acid.

Thin starches may be analysed by the general process given above for starch. The matter soluble in cold water consists chiefly of dextrin and dextrose The latter is estimated in the filtrate by means of Fehling solution If alcohol be added to another portion of the filtrate, the dextrin will be precipitated but not the dextrose The former may then be filtered off and weighed

But dextrin and dextrose can be determined more accurately in the following manner —

1. The dextrose is determined gravimetrically in, say, 50 c c of the filtrate by means of Fehling solution, weighing the cuprous oxide on a Gooch crucible

2 Fifty c c of the filtrate are placed in 100 c c flask together with 5 c.c. of hydrochloric acid, and the flask is heated in a water-bath for three or four hours, replacing the water lost by evaporation. This converts the dextrin into dextrose The contents of the flask are then cooled, made alkaline with sodium hydroxide, and diluted to 100 c c. with water The liquid is mixed and, if necessary, filtered Ten c c. of the filtrate, representing 5 c c of the original solution, are then treated with Fehling solution and the cuprous oxide collected on a Gooch crucible and weighed The difference between the two weights of cuprous oxide is due to the dextrose formed from the dextrin present. This is converted into dextrin by multiplying by the factor 0·4171

The method of Babington, Tingle, and Watson (*J.S.C.I.*, 1918, 257T) is very good. The following determinations are made: (*a*) Ash, (*b*) moisture; (*c*) dextrin gum, (*d*) insoluble starch; (*e*) reducing sugars, (*f*) total starch (100—(*a*+*b*+*c*)); (*g*) soluble starch (*f*—*d*), (*h*) non-reducing dextrin gum (*c*—*e*).

The method of procedure is as follows —

Dextrin Gum (*c*).—One gramme of the sample is warmed with 30 c c of water in a 100 c.c. flask till just gelatinised and then cooled quickly Fifty c c. of a saturated solution of barium hydroxide are then added. The contents of the flask are mixed, made up to 100 c c. with distilled water, and filtered. Fifty c c. of the filtrate are placed in a platinum dish and a drop of phenolphthalein solution, and normal hydrochloric acid is added till the mixture is just acid The pink colour is then restored by careful addition of barium-hydroxide solution. A weighed quantity (10 grammes) of dry washed sand is added and the water evaporated on the water-bath. The dish is then dried at 120° C. (to dehydrate the barium chloride) and weighed. The organic matter is then burnt away and the dish reweighed The difference between the two weights

gives the dextrin gum. The other determinations are made in the usual manner

Dextrin $(C_6H_{10}O_5)_n$.—When starch is heated to a temperature of 210° C. it is converted gradually into dextrin, the change being accompanied by the production of a yellow or brownish colour The reaction takes place at a lower temperature if the starch be previously moistened with a dilute solution of an acid Hydrochloric, nitric, and organic acids are all used for this purpose. Solutions of dextrin, together with dextrose, are obtained when starch is heated with a dilute acid or treated with a suitable enzyme Pure dextrin can be obtained by dissolving starch in moderately concentrated sulphuric acid, neutralising the solution and precipitating the dextrin with excess of alcohol. Malfitano and Moschkoff (*J.S.C.I.*, 1912, p 245) found that if starch be desiccated by drying in a vacuum over phosphorus pentoxide it is changed into dextrin, and that a greater yield is obtained in this way than by heating the starch to 100° or 130° C When the desiccation is carried so far that not only water of hydration is evolved but also combined water, the solubility diminishes That is, these authors regard dextrin as being formed from starch by the abstraction of loosely combined water, which is not part of the molecule They suggest that in starch the $C_6H_{10}O_5$ groups are linked together into complexes by molecules of water (H.OH), and that the withdrawal of these molecules on desiccation causes the breaking up of the complexes with the formation of simpler and more soluble molecules. When starch is heated with water, the breaking up of the complexes is the result of electrolytic dissociation and is not so complete

There are several different forms of dextrin, among which are amylodextrin, erythrodextrin, and acrodextrin They are distinguished by their reactions with iodine solution Amylodextrin gives a reddish-brown, erythrodextrin a red, and acrodextrin no colour

Pure dextrin is a white, tasteless, amorphous solid When examined under the microscope in the dry state, it is seen to retain the structure of the original starch granules, but directly it is moistened with water this disappears Dextrin is hygroscopic, and dissolves in its own weight of cold water, forming a viscous liquid with a high dextro-rotatory power (a_D=200) It is soluble in dilute alcohol, but is precipitated by a 50 per cent solution It contains from 8 to 12 per cent of moisture. When heated with potassium hydroxide acetic acid is split off, corresponding to from 15 to 24 per cent of potassium hydroxide It does not form a precipitate with tannic acid, but is thrown down from its aqueous solutions by ammoniacal lead acetate It is not precipitated by concentrated solutions of barium hydroxide When dextrin is heated, it becomes darker in colour owing to the formation of caramel This change is accelerated greatly by the presence of traces of alkalis or acids Cold concentrated sulphuric acid dissolves dextrin, but changes it quickly into dextrose When the mixture is warmed, charring takes place in the same way as with sugar or starch Hot nitric acid of 1·3 sp gr. converts dextrin into oxalic and other acids. When heated with dilute acids, dextrin is changed first into maltose and then into dextrose—

$$2C_6H_{10}O_5+H_2O=C_{12}H_{22}O_{11},$$
$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6.$$

Dextrin does not reduce Fehling solution.

Commercial dextrins are known as (1) white dextrin, (2) canary dextrin, (3) yellow dextrin. These, as their names indicate, differ in colour, but they also differ in composition White dextrin is the product of the limited action

of heat or acid on starch It contains much soluble and frequently unchanged starch When dissolved in hot water, the solution generally sets to a thick paste on cooling

Canary dextrin is made by carrying the process a little further The proportion of soluble starch is less than in white dextrin, and that of dextrin is proportionately greater. But traces of dextrose or maltose are also generally present

Yellow dextrin is the final product. It consists chiefly of dextrin, but contains more sugar than either of the other varieties

In addition to starch and sugar, commercial dextrins nearly always contain free acid

Dextrin gives an extremely soft finish, and it penetrates goods easily. But, owing to its hygroscopic nature, goods dressed with it are liable to have a damp, sticky feel. The type of finish obtained depends naturally upon the proportions of dextrin and unchanged, or partly changed, starch present. Many dextrins are identical with thin starches in properties Since small proportions of unchanged starch affect the result considerably, some care is necessary to obtain evenness in finishing. Sugars and acid form the chief danger attending the use of dextrins. If the dextrin has been made by an acid process, traces of acid will nearly always be left, and sometimes a considerable quantity is met with. When these dextrins are used tendering may result; but more generally discoloration, due to the action of the acid either on the material itself or on the sugars which generally accompany the dextrin No dextrin which contains both acid and sugar is safe to use where a fine white finish is required Although at first the colour may appear to be good, yet, on storing, a discoloration often develops Sugar is also objectionable, since its presence encourages the growth of organisms, especially yeasts and lactic ferments Thus, a dress made with a dextrin containing much dextrose sours more rapidly than it should, and owing to the deliquescent nature of dextrin the finished goods are also more liable to bacterial attacks

The following table, taken from Polleyn's *Dressings and Finishings*, gives the average composition of commercial dextrins –

	Prime Dextrin	Light Dextrin	Brown Dextrin
Dextrin	72 45	5 34	63 60
Dextrose	8 77	0 21	7 67
Starch	13 14	86 47	14 51
Water .	5 61	7 95	14 23

The Analysis of Dextrin.—The methods given for starch are equally suitable for dextrin

Glutinous and gelatinous stiffening agents are chiefly employed in connection with fabrics such as nets, veilings, and the like, the threads of which require considerable support (without any appreciable filling) in order to present the pattern in which the threads are twisted or woven in an effective manner, as the pattern is a most important feature in connection with such goods. Gums and glues were formerly used to a greater extent than at present in the finishing of heavier goods, on account of both their binding power with respect to filling materials and their stiffening properties, but they have been largely superseded

by starches. This has been in part due to the prices of the respective materials, and it is sometimes overlooked that under varying market conditions the advantage may be found to lie with the material which had once been discarded.

These materials can be manipulated to any extent as regards the degree of stiffness to be imparted, and varieties of gums are coming into extended use as assistants, as also to give an increased measure of body and toughness to the so-called pure finishes

Gelatin and Glue.—Both gelatin and glue are made from the same materials, viz, horn, bone, or skin, the difference between them being only in the condition of the raw material and the care exercised during manufacture. As a general rule, the lower grades of glue are made from bones, while the best glue and gelatin are derived from skins or the clippings thrown aside by tanners. Both skin and bone contain a nitrogenous body termed collagen or ossein, which, although insoluble in water, gradually undergoes hydrolysis on prolonged boiling, being changed into soluble glutin or gelatin This change is shown in the equation

$$C_{102}H_{149}N_{31}O_{38}+H_2O=C_{102}H_{151}N_{31}O_{39}$$

In the manufacture of glue from bones the fat is first extracted by means of benzine in a large extractor, and recovered The degreased bones are then heated with steam under pressure for some hours or sometimes in an open pan The solution thus obtained is run off, and clarified and bleached, after which it is concentrated and run into moulds to set. The jelly thus obtained, containing about 70 per cent of water, is cut into sheets, laid on wire netting and dried in a current of air till it contains about 15 per cent of water The clarification is commonly effected by the addition of a little alum This has the power of coagulating certain of the impurities, such as mucin, and these settling down carry much organic matter with them The bleaching agents used are either sulphur dioxide or hydrogen peroxide The former is used either as sulphur dioxide or as a hydrosulphite, while the hydrogen peroxide is made from sodium peroxide by treatment with dilute acetic acid. The concentration must be carried out rapidly at reduced pressure, since glue solutions rapidly deteriorate when boiled at ordinary temperatures

The process for skin glue is simpler, in that the skins are generally gently boiled by means of steam in an open copper, the liberated fat being skimmed from the surface as it rises

The purity and value of the final product depends very largely upon two factors, viz the condition of the raw material, and the care taken in manufacture to prevent excessive hydrolysis

When nitrogenous bodies, such as skin substance, are kept for any length of time they are gradually attacked by putrefactive organisms The first result of putrefactive bacterial action is to change the insoluble hide substance into glutin by hydrolysis The reaction does not stop here, however, but a second hydrolysis is caused, resulting in the breaking down of the complex glutin molecule into two simpler ones, known as gelatone peptones This change is shown by the equation

$$C_{102}H_{151}N_{31}O_{39}+2H_2O=\underset{\text{semiglutin}}{C_{55}H_{85}N_{17}O_{22}}+\underset{\text{hemicollin}}{C_{47}H_{70}N_{14}O_{19}}.$$

These are no longer colloidal bodies like glutin, but readily soluble and diffusible, they have no jellifying properties. Prolonged hydrolysis may even go further, resulting in the breaking up of these peptones into a mixture of

still simpler nitrogenous compounds, belonging to the class known as amino acids Among these are

Glycine	CH_2NH_2COOH
Leucine	$(CH_3)_2CHCH_2CHNH_2COOH$

Thus decomposed glue material contains, in addition to collagen, all these products of hydrolysis, and since they are not removed during manufacture, they will be found in the finished product

But this hydrolysis may also be caused during manufacture from perfectly sound material by over-boiling, or by the action of certain chemical reagents, such as acid or alkali

When a solution of gelatin is boiled for some time and allowed to cool, it will be found to form a weaker jelly than at first, and if the boiling be sufficiently prolonged, it will entirely lose its power of setting In the presence of such bodies as acids and alkalis these results are much more rapidly produced The changes due to boiling are quite analogous to those produced by putrefaction, and consist in the hydrolysis of the glutin into bodies termed gelatose, gelatone peptones and, ultimately, amino acids They are, of course, hastened by boiling under pressure

If the manufacture of glue or gelatin consisted only of the hydrolysis of collagen into glutin it would be a very simple operation, but these reactions proceed simultaneously, and all glues and gelatins contain nitrogenous compounds of at least three kinds, viz glutin, peptones, and amino compounds The problem of the manufacturer is to limit the hydrolysis, as far as possible, to the first stage, and the value of his final product is determined chiefly by his ability to do so The same factors determine also the classification into glue or gelatin Glue is merely gelatin in which the simpler nitrogenous compounds are present to a higher degree either owing to the nature of the raw material or the extent to which hydrolysis has proceeded during manufacture

There is no distinct line between the two bodies, and it often happens that a good glue is, except in the matter of colour, better in every respect than many gelatins This is seen in the following analyses —

	1. Good Gelatin	2 Pad Gelatin	3. Good Glue	4 Poor Glue.
	Per cent	Per cent	Per cent	Per cent
Water	14 00	14 00	14 23	16 23
Mineral matter .	1 58	1 75	1 33	2 75
Gelatin	80 00	75 00	78 08	64 35
Peptones and other nitrogenous bodies .	0 50	4 50	1 95	11 10
Non gelatinous bodies	3 92	4 75	4 41	5 55

In selecting a glue or gelatin we must then pay attention chiefly, not to the quantity of nitrogenous bodies present, but to their quality An analysis that gives merely the total nitrogen, assuming that it is all present in gelatin, is of very little use

Peptones when present in any quantity deleteriously affect the strength of the jelly which is formed Thus, in the above illustrations, the relative strengths of the jellies formed by dissolving the same weights of the substances in equal

volumes of water were 100, 65, 90, and 20 respectively A glue or gelatin which forms a weak jelly is never so good as one giving a strong jelly.

Moreover, peptones are very deliquescent, and a fabric dressed with them attracts moisture from the atmosphere and thus acquires a damp or sticky feel. It is also much more likely to become mouldy, since not only do peptones form an ideal germ food, but, owing to their deliquescent nature, the necessary moisture is always present

Lastly, the presence of peptone always increases the foaming power of a glue. It is very difficult, if not impossible, to get an even dress on a lace net with a foaming glue or gelatin

Glue sometimes contains another nitrogenous compound termed mucin, which also has very marked frothing powers. Mucin is obtained from various tissues, glands, and mucous membrane. It is soluble in alkaline solutions, but is precipitated by acids or alum One of the objects of clarifying with alum is to remove mucin, but it is not always easy to coagulate. Mucin is, perhaps, chiefly introduced by the accidental inclusion of cartilage with the glue material It has generally been supposed that cartilage when boiled yielded a glue-like substance, termed chondrin, containing about 15 per cent of nitrogen and having reactions similar to those given above for mucin Morner and Trotman (*J S.C I*, 1910, p 662) have, however, shown that cartilage on hydrolysis really yields a mixture of mucin and gelatin The following is an analysis of a glue *containing mucin which was used for dressing with bad results* –

Water	16 45 per cent
Mineral matter	2 22 ,,
Gelatin	55 07 ,,
Peptones, etc	14 21 ,,
Mucin	4 73 ,,
Non-gelatinous bodies	7 28 ,,

Other constituents of glue which require notice are acid and grease

Glue is generally bleached with sulphurous acid, and such glues are always acid In a good sample the acidity should not be more than 0 25 to 0 5 per cent., but it sometimes rises to 2 per cent. Excess of acid, if due to bleaching, may even cause tendering. It also causes hydrolysis during solution and so detracts from the strength

To make a glue solution the glue should be soaked overnight in cold water. The water is poured off next morning, and the swollen clear jelly is placed in water and gently warmed to about 30° C., at which temperature it dissolves readily In this way the risk of hydrolysis is minimised A good glue when soaked in cold water should absorb from five to seven times its weight in twenty-four hours, and form a firm, clear, sweet-smelling jelly Keeping a glue solution melted for any length of time should always be avoided If the temperature be high it will cause hydrolysis, while if low it will encourage the growth of putrefactive organisms which will also hydrolyse the gelatin and probably cause mouldiness subsequently.

Fat is rarely present in more than traces, but if there be more than 0·25 per cent it must be considered as an impurity. The same applies to soaps. The latter are, however, sometimes purposely added to certain special makes The following table gives the results of the analysis of a number of commercial samples of gelatins and glues used in finishing The term consistency denotes the strength of the jelly compared with that made from a standard gelatin under identical conditions, as measured by the weight required to break the surface. Non-gelatinous bodies are determined by difference.

	1.	2.	3	4.	5.	6.
	Per cent	Per cent.	Per cent.	Per cent.	Per cent	Per cent
Water	12·63	14 43	13·16	15·03	16 49	12 80
Mineral matter . .	1·50	1·87	1 34	1 74	2·22	1·76
Gelatin . .	76 30	77 42	74 23	68·76	55 07	64·76
Peptones and other nitrogenous compounds .	2 25	1·90	6 92	9·74	18·94	14·30
Non-gelatinous bodies .	7·32	4 29	4·35	4·73	7 28	6·38
Consistency . . .	85	90	60	30	20	22·5
Water absorbed . . .	4·08	4·85	4 00	3·00	2·75	3 70
Acidity . .	0 70	0 15	0·15	1·01	1·09	2 44

Properties of Glue and Gelatin.—Gelatin is insoluble in organic solvents such as alcohol, ether, benzene, and petroleum ether. It can be precipitated completely from its solutions by the addition of alcohol. Pure gelatin is also insoluble in cold water, but if it contain soluble and diffusible impurities these pass into solution When soaked in cold water gelatin absorbs from five to six times its weight, forming a firm, clear jelly. When this jelly is warmed it melts, forming a clear colloidal solution which sets again on cooling The firmness of the jelly depends upon the quality of the gelatin or glue. With a good gelatin a 2 per cent solution sets, but in the case of a low-grade glue more than 10 per cent is necessary

Solutions of gelatin are precipitated by tannic acid The insoluble gelatin tannate, or leather, has not, however, a constant composition Gelatin is precipitated, also, when its aqueous solutions are saturated with sulphates of ammonium, zinc, or magnesium, and also by phosphomolybdic acid, phosphotungstic acid, or a large excess of mercuric chloride It is also precipitated by a saturated solution of picric acid if added in excess But it is not precipitated by copper sulphate or potassium ferrocyanide, differing in this respect from the proteins The halogen elements also precipitate gelatin from its solutions If chlorine gas be passed into a solution of gelatin, insoluble chloramines are formed and the gelatin is completely precipitated When bromine or iodine is used the precipitation is not complete

Gelatin combines directly with formaldehyde, from 4 to 4·8 per cent being taken up The compound "formogelatin" is insoluble in both cold and boiling water If a cotton fabric be soaked in a solution of gelatin and then in formalin it becomes perfectly waterproof when dried Small quantities of formaldehyde up to 1 in 10,000 act as a preservative but do not produce this insoluble compound.

Small quantities of potassium bichromate or salts of chromium act in a similar manner after exposure to light Waterproof dressings may be produced in this way

When gelatin or glue is dissolved in a hot concentrated acetic acid, the solution does not gelatinise when cooled, but forms what is known as a liquid glue. Liquid glues can be made also by many other methods, such as (1) heating with small quantities of acids or alkalis; (2) heating with certain phenols and sulphonic acids, such as phenol, cresol, and naphthalene sulphonic acid, (3) heating with solutions of certain salts, such as calcium chloride, calcium nitrate, calcium thiocyanate, etc., (4) treating it with proteolytic enzymes.

Both glue and gelatin are very susceptible to alkaline hydrolysis, even small

quantities being sufficient to lower the melting-point of the jelly on cooling gelatin cause liquefaction.

The Detection of Gelatin.—The reaction between gelatin and tannic acid is very delicate, but is given by so many other bodies that it is of little use. The picric-acid test is capable of detecting 1 part of gelatin in 10,000 of water. A little of the solution to be tested is treated with a few drops of acid mercuric nitrate solution and warmed gently. This coagulates proteins, which react also with picric acid The solution is filtered and the clear filtrate treated with a cold saturated aqueous solution of picric acid If gelatin be present a precipitate is formed which dissolves at first, but becomes permanent when excess of the reagent is added. The mercuric nitrate solution is made by dissolving 1 gramme of mercury in twice its weight of concentrated nitric acid (sp. gr 1·42) and diluting the solution to five times its volume with water

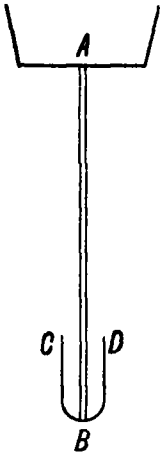


Fig. 195.—Apparatus for determination of breaking strength of jelly

The Testing of Glue and Gelatin.—More information can be obtained from physical than from chemical tests, and the former are commonly relied upon in the selection of both glues and gelatins The chief of these are—

1. *Water Absorbed.*—A weighed piece of the sample (about 5 grammes) is suspended by means of a fine silk thread beneath the surface of cold water in a beaker for forty-eight hours The water is then strained off and the jelly weighed From the increase in weight the water absorbed is calculated

Good gelatins absorb at least seven times their weight of water, and a glue from four to five Bad samples may become slimy or form a solution The jelly formed should be clear and firm and devoid of smell.

2 *Strength of Jelly of Consistency.*—(a) *Lapowitz Method* Ten grammes of the sample are soaked overnight in about 50 c c of cold water. The jelly is then melted, the solution made up to 100 c c and allowed to set in a small cylinder or pot A small cylindrical metal cup is then placed on the surface of the jelly To this is attached a vertical metal rod which passes through a support which keeps the apparatus in a vertical position At the top of this rod is a second cup, into which shot is poured until the lower cup sinks to a certain point in the jelly, the weight of the shot together with that of the instrument gives the breaking strength of the jelly. Reliable results may be obtained with the apparatus shown in fig 195, where CD=½ inch and AB - 9 inches

(b) *The Finger Test.*—Ten grammes of the glue are dissolved in 100 c.c of water and allowed to set in a cylindrical pot. In a number of exactly similar pots varying weights of a standard glue or gelatin (Coignet's Gold Label) are dissolved in 100 c.c of water and allowed to set side by side with the glue When these have all set, the strength of the glue jelly is matched against them by lightly pressing the surface with the finger-tips, and that particular strength of gelatin noted which offers the same resistance to the finger as the glue. The strength of the jelly is then expressed as a percentage of the standard used. For instance, 10 grammes of glue gave a jelly equal in consistency to that obtained from 3·5 grammes gelatin. Hence the consistency of the glue is said to be 35.

3 *Viscosity Test.*—According to Bogue (*The Chemistry and Technology of Gelatin and Glue*, p. 308), the viscosity of a glue solution is the most valuable physical test. This is determined by noting the time required for a solution to

run out of a pipette under standardised conditions A 25 per cent solution at 80° C. is used. Any suitable pipette may be employed, but it is usual to use one which, when filled with water, requires fifteen seconds to become empty. The number of seconds taken by a glue solution divided by fifteen then gives its viscosity compared with that of water For accurate results the pipette should be kept at a constant temperature in a bath of water. Archbutt's viscometer (fig 196) is a very convenient form of apparatus.

A stout glass burette with a short stem is graduated to 25, 50, and 100 c.c, reckoning from a zero mark placed a little below where the jet begins. It is surrounded by a water-jacket ending at the bottom in a neck closed by a thin rubber cork, pierced for the stem of the burette The jacket is closed at the top by a large rubber bung with holes to admit the burette, a funnel tube for pouring in water, thermometer, stirrer, and tubes for the entrance and escape of steam Near the bottom of the jacket is a side aperture for running out water The clean burette is pushed through the large bung until its stem projects about $\frac{3}{16}$ inch below the cork, but not beyond the glass neck So adjusted, chilling of the glue during its outflow is reduced to a minimum. For ordinary glues a 25 per cent solution at 80° C is convenient for viscosity determinations The jacket is filled with water at that temperature, the jet of the burette plugged with a peg of soft wood, and the glue solution, previously heated to 80° C., poured into the burette to a point above the 50 c c mark When the glue is exactly at 80° C., determined by stirring with a thermometer, the peg is withdrawn from the jet and the glue allowed to run out A stop-watch is started the moment the surface of the glue solution reaches the 50 c c. mark and stopped the moment it passes the zero mark, the time taken being compared with that required by standard glue, water, or an oil of known absolute viscosity measured by the same instrument.

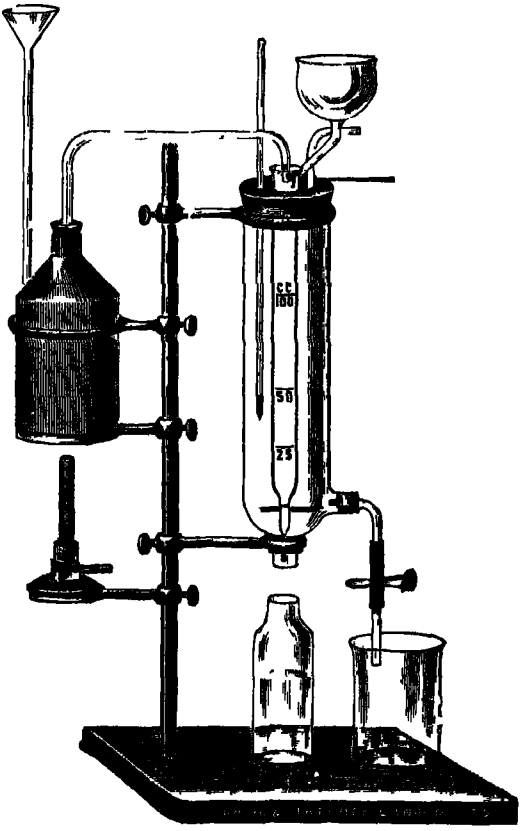


FIG 196.—Archbutt's viscometer

Chemical Analysis.—For use in dressing or sizing the physical tests just described are generally sufficient to give all the information required. A chemical analysis includes the determination of (1) moisture, (2) ash, (3) total nitrogen. Moisture and ash are determined in the usual way and nitrogen by

the Kjeldahl process The total nitrogen multiplied by 5·56 gives gelatin The sum of the water, ash, and gelatin deducted from 100 gives non-gelatinous bodies

Acidity is determined by soaking a weighed quantity of the sample overnight in cold distilled water, dissolving at a low temperature, and titrating with decinormal sodium hydroxide, using phenolphthalein as indicator It may be mentioned that the pH value of a good sample when tested by a suitable indicator should be from 5 to 5·5

Both glues and gelatins generally contain sulphurous acid as a preservative This is detected by distilling some of the jelly with steam into bromine water a d then testing the distillate for sulphuric acid The process may be made quantitative also Twenty-five grammes of the sample are placed in the distilling flask shown in fig 197, covered with air-free distilled water, and allowed to stand for about four hours Bromine water is placed in the beaker, the end of the adapter dipping beneath its surface When the gelatin has swollen up the water in the

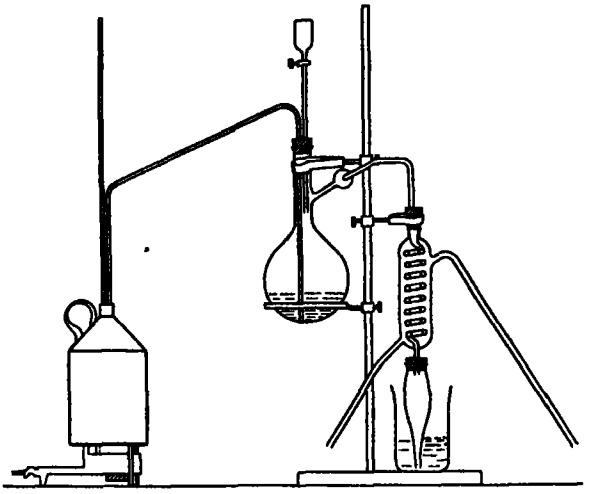


FIG 197

boiler is heated and allowed to boil for some minutes to expel air The steam is then passed through the distilling flask for about thirty minutes Some hydrochloric acid is then added to the distillate, which is boiled till the excess of bromine is expelled Barium chloride solution is then added, and the precipitated barium sulphate filtered off and weighed in the usual manner If combined sulphur dioxide be required, a few drops of phosphoric acid are run into the flask by means of the tap funnel before passing in the steam

Casein. When milk is allowed to ferment under the influence of the lactic acid ferment, it curdles owing to the precipitation of casein The same result may be obtained by treating the milk with rennet or a dilute acid If the curd be filtered off and washed, fairly pure casein is obtained The milk does not itself contain casein, but an albuminoid body termed caseinogen, which is readily transformed by acids, and ferments into insoluble casein. This caseinogen may be obtained from milk by removing the fat by means of a separator and saturating the liquid with magnesium sulphate, which causes its precipitation The precipitate when dissolved in distilled water and acidified yields casein. Casein is readily obtained from skim milk by treating it with 0·1 per cent. of

acetic acid. The resulting precipitate is filtered and washed. It is then dissolved in dilute caustic soda and filtered till nearly clear, after which it is again acidified. The resulting precipitate of casein is collected, washed, and dried If a fat-free powder be required it should be washed with ether before drying.

Casein is a protein, but differs from many others in containing more phosphorus and in not being coagulated on boiling But, like other proteins, it is precipitated by tannic acid, phosphotungstic acid, phosphomolybdic acid, mercuric and cupric salts It is precipitated completely, also, by adding excess of alcohol to its faintly acid solution Pure casein is a white amorphous powder, which swells up when soaked in cold water but does not dissolve. It is, however, soluble in dilute solutions of caustic alkalis It dissolves also in solutions of ammonia, alkaline carbonates, borax, and sodium phosphate. If a dilute acid be added to an alkaline solution of casein the protein is precipitated as the acid salt This compound is soluble in hydrochloric acid containing less than 0·1 per cent of real acid, but is insoluble in acid of moderate strength Concentrated hydrochloric acid dissolves it, and when the solution is heated a violet colour is produced

Casein, like other proteins, is amphoteric, *i e* acts both as an acid and a base. It has itself a faintly acid reaction If casein be dissolved in sodium hydroxide, carbonate, or phosphate or calcium hydroxide in the calculated quantities, and the solutions be evaporated *in vacuo*, the corresponding casein salts are obtained in the form of white powders When a solution of casein is mixed with formaldehyde and dried, a transparent insoluble mass is left similar to formaldehyde gelatin Casein may often be used for stiffening with good results. It may be first soaked with water till swollen and then added to the remainder of the dressing mixture A better plan is to dissolve it in a little mild alkaline solution, such as borax or sodium carbonate Goods may be treated with this solution and subsequently passed through an acid bath to coagulate the casein, after which they are washed and dried If a waterproof dress be required, formaldehyde casein may be employed. The solution of the protein is mixed with about 2 per cent of formalin and the goods afterwards slowly dried, when insoluble formaldehyde casein is obtained, or the casein may be first applied and the goods subsequently treated with a formaldehyde solution and dried In using commercial solutions of formaldehyde any free acid must always first be neutralised

Gums.—These bodies occur in the juices of plants and are generally obtained as exudations. They are, as a rule, tasteless, almost colourless bodies with highly marked colloidal properties They generally swell in contact with cold water, and the jelly when warmed forms a semi-solution Some of them gradually dissolve in cold water A number of bodies are classed as gums which have, however, not much in common Thus pectin, a natural constituent of cotton, is generally considered to be a gum. Algin, gelose, gum tragacanth, and gum arabic are of use all to the finisher and will be briefly described.

Algin occurs in various seaweeds, from which it is prepared as a thick viscous solution containing from 90 to 95 per cent. of water It dissolves, however, more readily in dilute alkaline solutions, such as sodium carbonate. If such a solution be acidified, a whitish precipitate of alginic acid is thrown down. Solutions of algin are also precipitated by many metallic solutions, such as zinc sulphate and calcium chloride, insoluble compounds of the metal with alginic acid being formed. In using algin for dressing it is better to employ one of these reactions. The fabric is first treated with a solution of algin and then with dilute acid or a solution of a metallic salt, and subsequently washed and

dried. A solution of algin behaves very much like one of casein. Like casein, it contains nitrogen, but it is not precipitated by tannic acid or mercuric chloride or formalin. An aqueous solution of algin has a high viscosity.

Algin is met with either as a mucilage or a dried horn-like mass capable of forming a mucilage with water. The following are analyses of typical samples .—

	Mucilage	Dry Material
	Per cent.	Per cent.
Water . . .	83 41	18 90
Mineral matter	3 55	16 88
Algin . . .	13 04	64 22

Gelose is made from a Japanese seaweed frequently sold under the name of agar If this weed be finely powdered and boiled for some hours with water it disintegrates and dissolves Upon cooling the solution it sets to a hard jelly The setting power is very remarkable, 1 part in 500 of water being sufficient to form a jelly If it be heated for a long time with water or dilute acid it undergoes hydrolysis and loses its power of setting

Tragacanth is the dried exudation of *Astragalus gummiger*, which grows in Lebanon, Syria, Central Asia, and America The gum occurs in two forms (1) leaf gum in small, irregular curved strips with a crinkled surface, and (2) vermicelli gum in cylindrical sticks (Stocks and White, *J.S.C.I.*, 1903, p 5)

It varies in colour from white to yellow or brown and grey When boiled with water it gives up about 60 per cent of its weight capable of being removed by filtration With cold water it gradually swells and forms a thick jelly-like mass which forms a partial solution on warming, settling to a jelly when cooled again. Its solution has a very high viscosity, greater than that of gum arabic, and only exceeded by that of Iceland moss It does not form a clear jelly, but is somewhat opaque with white specks scattered through it These consist of oval cells containing some starch granules similar in appearance to those of rice or maize. The water content of tragacanth varies considerably, rising as high as 26 per cent. According to Stocks and White, the dry gum mucilage contains—

Carbon . . .	42 33 per cent
Hydrogen . .	5 59 „
Oxygen .	47 85 „
Nitrogen	0 05 „
Ash . .	4 18 „

These figures agree fairly closely with the formula $C_6H_{10}O_5$. Tragacanth is too expensive for very general use, and the cheaper varieties are often adulterated

Tragasol is made from the seed of the twist bean, the fruit of *Ceratonia siliqua* The seeds are first split and are then mechanically separated into husks and cotyledons. The cellulose tissues of the latter contain the gum, which is extracted by careful kneading with hot water. The solution is strained or filtered, and treated with a preservative. The gum forms a stiff, whitish, transparent jelly, somewhat similar to tragacanth, containing no starch, but a considerable amount of nitrogen (equal to 2·4 per cent. of albuminoids). It does not dissolve in water, but, when stirred with it, appears to take up the water,

the mass remaining as stiff as before It mixes most readily with water at a temperature of 100° to 140° F It is important that it should be thoroughly mixed with the water before use It is a valuable binding agent for mineral fillings and starch, and gives cloth a smooth, tough, leathery feel.

Irish moss is a variety of seaweed collected in Ireland and Scotland. When heated with water, about 60 per cent of it goes into solution If this be filtered through linen or canvas, the solution sets on cooling to a fairly stiff jelly The moss should be washed before use, as it is liable to contain a considerable amount of salt and other impurities The following analysis shows an average commercial sample —

Water	13 28 per cent
Soluble matter	44 00 ,,
Insoluble matter	41 52 ,,
Mineral matter	1 20 ,,

Irish moss contains a large quantity of pectin, which may be precipitated as pectic acid by acidifying an aqueous extract of the substance It does not give a hard finish, and is no use for goods that have to be calendered under pressure, since the finish breaks down under calendering, but it is useful for lightly dressed goods, producing a so-called natural finish It imparts a bulky feel, with a high degree of softness, and an absence of papery feel A 0·75 per cent decoction is particularly good for dressing flannelette, in which heavy dressings tend to lay the nap and dust out during the raising process It mixes well with other finishes, and tends to prevent the bleeding of the dyestuffs in washing The moss should be steeped in water for twelve hours and boiled for two, and it is desirable to use an antiseptic (*J S C I*, 1904, p 422)

Iceland moss contains a gum similar to pectin and is used in much the same way It is more soluble in water than Irish moss, containing about 70 per cent of soluble matter consisting chiefly of pectin

Gum arabic is the dried exudation obtained chiefly from trees of the acacia species growing in the Soudan Its chief constituent is the calcium salt of arabic acid, $C_{89}H_{142}H_{74}CaO$ When treated with dilute acids it splits up into a sugar similar to glucose (arabinose) and arabinosic acids Gum arabic is soluble in water, forming a thick viscous solution from which it is thrown down by alcohol, alkaline silicates, borax, mercuric chloride, and ferric salts It is the only gum which is completely soluble in water, requiring about one and a half times its own weight Its adhesive properties are increased by the addition of alum to its solution, a mixture of aluminium arabinate and calcium sulphate being produced

A solution of the gum has a high viscosity, and the lower grades can be differentiated by this means There are many different qualities of gum arabic, which are generally distinguished by names denoting their origin, such as picked Turkey, white Sennaar, gum Senegal, Cape gum, etc, and Indian gum (Hurst, *Dictionary of Chemicals and Raw Products*) The true gum arabic comes only from the Soudan The varieties differ in solubility in water, and in the strength of the mucilage or jelly which they form

Carnauba wax belongs to the vegetable waxes, which are produced as exudations from the leaves of trees It is obtained from a South American palm It is a very hard brittle substance with a slightly yellowish colour, though it may be bleached quite white. It has a remarkably high melting-point, ranging from 80° to 84° C It does not readily mix with water, but in the presence of an alkaline carbonate an emulsion may be obtained which has very marked stiffening properties It may be saponified by prolonged boiling with alkali, and

the fatty acid may then be precipitated in a fabric. The fatty acid (carnaubic) has a melting-point of 72·5° C. The zinc soap made by treating a solution of the sodium soap with zinc sulphate is a white substance, which, unlike other soaps, does not decompose on keeping, and is a very good filling or stiffening material. It is fairly soluble in benzene.

Softening Agents—*Soap.*—The dangers attached to the use of soaps have already been indicated If soap be used, only the best should be employed, and such as have nearly colourless fatty acids Soap is frequently used as a lubricating agent in finishing mixtures, although in the presence of lime compounds it is comparatively useless for this purpose; a clear white soil, such as lard oil or cocoa butter, is in all cases preferable In this connection mention may be made of certain so-called "soluble oils," which are often merely solutions of soaps in water, the latter generally amounting to 90 per cent. A good soluble oil is *turkey-red oil*, which is largely used in dyeing cotton goods and has a softening effect.

Turkey-red oil is made by sulphonating castor oil (p 372) The value of a sample depends on the percentage of fatty matter present, which is usually about 50 per cent Owing to its acid nature it commonly contains iron as an impurity. The use of turkey-red oil as a "capillarising" agent in both the soda boil and the chemic has already been mentioned

The percentage of fatty matter in turkey-red oil can be determined by decomposing a weighed quantity with acid and extracting with ether in a separating funnel

Oils.—Many oils and some waxes are used as softening agents, including tallow, lard oil, castor oil, cocoa butter, ceresin, Japan wax, and petroleum jelly

Petroleum jelly is a mixture of paraffin wax and petroleum It is a white, soft mass with a melting-point of about 40° C It is, of course, inflammable, and has sometimes a low flash-point.

Ceresin is a wax obtained from a bituminous mineral termed ozokerite, which is found associated with petroleum Ozokerite contains, besides ceresin, mineral matter, hydrocarbons, earth, and water The refined product or ceresin is a yellow or white substance resembling beeswax, but, unlike beeswax, is completely unsaponifiable. Its melting-point varies from 60° to 78° C. It is sometimes adulterated with such bodies as paraffin wax, bleached rosin, or carnauba wax

Japan wax is obtained from the berries of a Japanese plant It is a yellowish, hard substance, melting at about 50° C It is insoluble in cold, but dissolves in boiling, alcohol, crystallising from the solution on cooling It is readily soluble in ether, petroleum, and other organic solvents It forms emulsions readily when shaken with hot water or water containing a little alkali, such as borax Japan wax contains about 1 per cent of unsaponifiable matter It consists largely of palmitin and free palmitic acid, together with small quantities of other acids, such as Japanic acid, $C_{19}H_{38}(COOH)_2$. The free fatty acids amount to about 10 per cent It is sometimes adulterated with water, starch, tallow, and other fats Genuine Japan wax has a very low iodine value not exceeding 15 When saponified with potassium hydroxide it yields glycerol. It is not, therefore, a true wax but a fat.

Cocoa butter is pressed from cocoa beans. It is a white or yellowish-white solid mass which melts at about 30° C. It does not readily become rancid, but has a characteristic smell. It contains only traces of unsaponifiable matter, has an iodine value of 34, and the titer of its fatty acids is 48° to 49° C.

Lard oil is a clear, colourless oil obtained by subjecting ordinary lard

pressure, the residue being lard stearin. The melting-point of lard oil varies from 10° to 12° C., being liquid at ordinary atmospheric temperatures It should contain only traces of free fatty acids and should not become rancid on keeping.

Tallow is obtained principally from beef and mutton fat. It is a white, tasteless substance, melting at from 44° to 48° C. Impure tallow has sometimes a yellowish colour. Unless it contains impurities it does not readily become rancid. It should not contain more than 4 per cent. of free fatty acids It consists of approximately equal proportions of triolein and tristearin, the free fatty acids having a titer of about 44° C. It should contain no water nor mineral matter, and less than 1 per cent. of unsaponifiable matter Its iodine value is about 40 to 45.

Castor oil is obtained from the seeds of *Ricinus communis*. It is a colourless or pale yellow oil, sharply distinguished from most other oils by its high specific gravity, viscosity, and solubility in alcohol. It is insoluble in petroleum. Its specific gravity varies from 0·960 to 0·964, and its viscosity is higher than that of all oils except rosin oil and blown oil. It is very readily saponified by alkalis and forms good emulsions It is largely used in the manufacture of so-called soluble oils and as a softener

Proprietary Softening Mixtures.—These are very numerous, and they generally consist of varying quantities of soap, cocoa butter, or other oil, made into emulsion or paste with water They should always be bought upon the results of analysis The following examples will illustrate the variations met with in this class of compound —

	1	2.	3	4
	Per cent	Per cent	Per cent	Per cent
Water	18 9	80 6	91 7	89 4
Unsaponifiable oil	55 6			
Saponifiable oil	.	1 0	4 0	
Soap	25 5	18 4	4 3	10 6

The Analysis of Oils used as Softening Agents.— The purity of an oil can be ascertained generally from the determination of its iodine value, and the percentage of unsaponifiable matter, water, and mineral matter In the case of solid fats the melting-point is also of assistance, and in some cases the flash-point is important. The determination of free fatty acids gives a measure of the rancidity of an oil.

Water.—About 5 grammes of the oil are weighed in a flat dish provided with a short piece of glass rod to act as a stirrer. The dish is then heated in an oven, the contents being stirred occasionally to assist the liberation of the water.

Mineral Matter.—From 5 to 10 grammes are burnt carefully in a weighed platinum or silica dish and finally ignited till no more organic matter is left.

Matter Insoluble in Petroleum Ether.—A weighed quantity of the oil is dissolved in petroleum ether and the solution filtered through a weighed Gooch crucible. The flask and filter are washed several times with warm petroleum ether, after which the crucible is dried and weighed. All oils except castor oil should be completely soluble in petroleum ether. In the case of castor oil ether should be used as the solvent.

Free Fatty Acids.—From 1 to 2 grammes of the oil are warmed in a flask with neutralised spirit to dissolve the free fatty acids. A drop of phenolphthalein

solution is added, and then decinormal sodium-hydroxide solution till a faint pink colour is produced. Each cubic centimetre of alkali used is equivalent to 0·0282 gramme of oleic acid

Unsaponifiable Matter.—This determination has been described on p. 264.

Iodine Value.—This is one of the most important tests for the purity of an oil It is a measure of the unsaturated fatty acids present The method of determination has been described in Chapter XIX

Melting-point.—The capillary tube method is generally convenient. The following method of determination is recommended by Archbutt and Deeley (*Lubrication and Lubricants*, p 194) —

The capillary tubes, which are made by drawing out soft glass tubing, should be very thin-walled, about 10 cm. long and 1 mm. in internal diameter They are left open at both ends. One end is dipped into the melted substance until enough has risen to fill about 1 cm of the tube, which is then laid aside in a cool place for several hours, preferably overnight, for the substance to solidify and regain its normal melting-point The other end of the tube is then held for a moment in a small flame and, while hot, is pressed against a bar of wood, W (fig. 198), coated with sealing-wax, by which means four or more of such tubes may be supported in a beaker as shown in the sketch The beaker is placed upon a disc of asbestos millboard over a burner, and a thermometer, T, held by a clamp or suspended by a cord, is placed with its bulb close to the filled ends of the capillary tubes The water in the beaker is then slowly warmed up and continually stirred by the glass stirrer, S, and the temperatures at which the substances melt and rise up the capillary tubes are recorded The mean of two experiments in separate tubes, which should closely agree, is taken as the melting-point of the substance

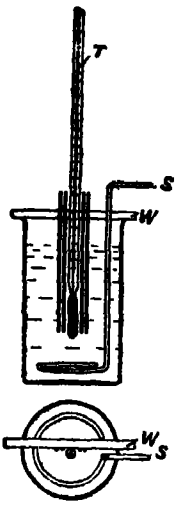


Fig 198 – Capillary tube method for determination of melting-point

Blueing Materials.—*Ultramarine* is a mixture of aluminium and sodium silicate with polysulphides of sodium A little is obtained naturally from lapis lazuli, the bulk being manufactured by igniting a mixture of silica, china clay, caustic soda, sodium sulphate, and rosin, the proportions varying according to the nature of the product required Its composition is approximately—

Silica . .	40 88
Alumina	24·11
Sulphur .	13 74
Oxide of sodium	15 61
Water .	2·60

It is very rarely adulterated, but different samples have very different colouring powers, depending upon the composition and fineness. The colouring power can be determined by diluting it with a neutral white powder, such as kaolin, until it has the same tint as a given quantity of a standard compound; or Lovibond's tintometer may be employed, in which case the powder is replaced by a set of standard glasses having definite colours. When treated with chlorine, ultramarine gives rise to a red-coloured compound. It is important, therefore, that goods should be quite free from chlorine if used with this pigment. Its colour is also destroyed by dilute acids, with the evolution of sulphuretted hydrogen.

Smalt is essentially glass coloured with oxide of cobalt, and is obtained by fusing a mixture of silica, potash, and oxide of cobalt. The depth of colour depends upon the quantity of cobalt oxide present. It is sometimes adulterated with ultramarine or barytes. It should, of course, be very finely ground, and its colouring powers tested, as with ultramarine.

Smalt and ultramarine are sometimes replaced by aniline dyes, or indigo, but these are not so fast. Occasionally so-called smalt consists of ground gypsum or barytes, coloured with a dye. The following analyses show the proportions of cobalt oxide found in commercial smalt :—

	Cobalt Oxide
No 1 .	7 57
No 2 .	9 03
No. 3	9 08

Antiseptics are bodies which delay the growth of bacteria. The name disinfectant refers to those which kill both bacteria and their spores. There is no definite distinction between the two classes, since many bodies are disinfectants in large and antiseptics in small doses. Chlorine is a powerful disinfectant on account of its oxidising power. Since, during its action, it becomes changed to hydrochloric acid, it has not a lasting effect. The same is true of other oxidising agents and sulphur dioxide, which is a reducing agent The phenols, salicylic and benzoic acids, boric acid, and formaldehyde, being less readily changed, have a more lasting effect Certain metallic salts, such as mercuric chloride or zinc chloride, potassium nitrate, sulphate of copper, have also a preserving effect. Although the use of preservatives in finishing mixtures is in many cases very desirable, there are not many antiseptics suitable for this purpose. Salicylic acid and benzoic acid are often precluded by reason of the fact that they form coloured compounds with even traces of iron Copper compounds can be used in some cases, formaldehyde in others, but, in general, the safest is boric acid.

Formaldehyde, HCHO, is made by the action of oxidising agents on methyl alcohol (CH_3OH)—

$$HCH_2OH+O=HCHO+H_2O$$

The vapour of methyl alcohol, mixed with air, is passed over a heated platinum spiral, and the product condensed in water, when a solution of formaldehyde is obtained The compound is only known in the gaseous state When an aqueous solution is concentrated or evaporated over sulphuric acid, the aldehyde is polymerised, forming crystals of para-formaldehyde, $(CH_2O)_2$ Formaldehyde has a penetrating odour and powerful antiseptic properties. It is generally sold under the name of formalin, which is a 40 per cent. solution of the gas. An important property is its power of combining with ammonia to form hexamethylene tetramine $(CH_2)_6N_4$—

$$6HCHO+4NH_3=(CH_2)_6N_4+6H_2O.$$

It acts in a similar way with proteins, gelatin, and bodies containing an NH_2 group. If cotton be dressed with gelatin containing formaldehyde, the gelatin becomes hard and insoluble on drying, and is very resistant to the attacks of bacteria. Formalin does not, however, lend itself to other dresses so well, as it is quickly lost by evaporation.

Boric acid, H_3BO_3, occurs in natural jets of steam (suffioni) which escape from the earth in certain volcanic districts, notably in Tuscany. The condensed steam collects in pools and is concentrated till the acid crystallises out. It is a

white, lustrous substance with a soapy feel. When neutralised with carbonate of soda, borax, $Na_2B_4O_710H_2O$, is obtained. Boric acid is not very readily soluble in water It may be added with safety to most dresses, but is not of much use in a proportion of less than 0·25 to 0·5 per cent.

Copper sulphate, $CuSO_45H_2O$, or blue vitriol, is made by dissolving copper oxide in sulphuric acid and crystallising the solution. It forms large blue triclinic crystals, when heated to 100° C it crumbles to a white powder, having the composition $CuSO_4H_2O$. If this residue be heated to about 200° C., it gives up the fifth molecule of water, anhydrous copper sulphate being obtained. Copper sulphate dissolves readily in water, forming a blue solution When this solution is treated with a caustic alkali, a bluish precipitate of copper hydrate is obtained, while the corresponding carbonate is thrown down on the addition of sodium carbonate. With ammonia the hydrate redissolves, forming a deep blue solution Copper salts inhibit the growth of moulds to a limited extent, but not of putrefactive bacteria They cannot be used with dressing mixtures containing soap, as an insoluble copper soap is at once thrown down.

Salicylic Acid, $C_6H_4\begin{cases}OH\\COOH\end{cases}$.—There are three hydroxy-benzoic acids, of which the ortho-compound or salicylic acid alone has any commercial importance It occurs in salicin, a glucoside found in willow bark It is generally made from sodium phenate, C_6H_5ONa, by treatment with carbon dioxide. When sodium phenate is treated with carbon dioxide, direct union takes place, with the formation of sodiumphenylcarbonate, $C_6H_5OCOONa$ When this compound is heated to 130° C it undergoes molecular transformation, producing sodium salicylate, $C_6H_4OHCOONa$, phenol being also produced, in accordance with the equation

$$C_6H_4(OH)COONa+C_6H_5ONa=C_6H_4ONaCOONa+C_6H_5OH$$

The reaction depends upon the presence of unchanged sodium phenate If, however, sodium phenate be heated with carbon dioxide under pressure, the sodium salicylate is produced unaccompanied by phenol.

Salicylic acid is a white, acicular, crystalline compound with a sweetish taste, melting at 156·75° C When gently heated to 200° C. it sublimes [illegible] and phenol When boiled with water it gradually volatilises. It is not very soluble in hot water, and sparingly in cold At ordinary temperatures 1 part of the acid requires 550 of water, and about 13 at 100° C It dissolves in 198 parts of glycerin, and is also readily soluble in alcohol, ether, and other organic solvents. It dissolves in alkaline solutions, such as sodium and potassium hydrates, forming salts known as salicylates. When treated with excess of bromine water it gives a precipitate in accordance with the equation

$$C_6H_4OHCOOH+4Br_2=C_6H_2Br_3OBr+CO_2+4HBr.$$

Salicylic acid has valuable antiseptic properties, from 5 to 10 grains to the pound being generally sufficient to inhibit putrefaction in mixtures that have been boiled. When used, however, with dressing mixtures made up at a moderate temperature, much larger quantities are necessary, viz. from 30 to 50 grains per pound

It forms a compound with formaldehyde, and hence these bodies should not be used together. The chief test for salicylic acid is the formation of a characteristic violet coloration on the addition of a solution of an iron salt.

This reaction makes its use sometimes inadvisable for lace goods, and freedom from iron must be first ensured

According to Allen, there are three distinct qualities of commercial salicylic acid, of which the "ordinary" or cheapest variety is the only one which would be used in dressing The chief impurities liable to be met with are phenol, cresol, potassium sulphate, and, occasionally, such adulterants as starch, gypsum, etc.

Phenol or *carbolic acid*, $C_6H_5(OH)$, is prepared from the fraction of coal tar distilling between 150° and 200° C This is neutralised with caustic soda and the solution separated from the undissolved oils It is then acidified with sulphuric acid, when the phenol is liberated and rises to the surface, forming an oily layer.

The reactions involved are—

$$C_6H_5OH+NaOH=C_6H_5ONa+H_2O,$$
$$2C_6H_5ONa+H_2SO_4=Na_2SO_4+2C_6H_5OH.$$

The crude acid thus obtained is distilled, and the portion coming over near 182° C collected separately and cooled in a freezing mixture, when the phenol crystallises out The crystals are separated by means of a centrifugal machine As indicated above, phenol is also obtained when salicylic acid is strongly heated in a retort

Phenol is a colourless crystalline compound, the crystals of which are needle-shaped, and melt at 42 2° C , forming a colourless liquid which boils at 182° C It has a strong burning taste and rapidly destroys the skin When exposed to the air it absorbs moisture, giving rise to a hydrate of the composition $2C_6H_6O + H_2O$, the hydrate melts at 17 2° C

Phenol is only sparingly soluble in cold, but dissolves readily in hot, water. The solution, when neutralised with alkalis, gives rise to compounds known as phenates, such as sodium phenate, C_6H_5ONa. It is readily soluble in organic solvents A solution of phenol coagulates solutions of albumin in the same way as acids It gives a precipitate with chlorine or bromine, hydrogen being displaced by halogen—

$$C_6H_5OH+Br_2=C_6H_4BrOH+HBr$$

When excess of the reagent is added, a further reaction occurs, forming tribromophenol, $C_6H_2Br_3OH$. Phenol has powerful antiseptic properties It is very useful with gelatin dresses. It may be used in the proportion of about 1 part in 1000

It is generally sold on a guaranteed percentage of tar acid It may contain neutral oils, which have only very limited antiseptic powers, and are further liable to cause discolorations with cotton goods. It gives a violet colour when treated with a solution of a ferric salt and a deep blue colour with hypochlorites in the presence of alkalis, or red in acid solution These reactions have, of course, their significance in the use of phenol for preserving bleached cotton goods

Although a powerful antiseptic, its smell makes phenol difficult to use for textile fabrics Sodium phenate is an equally good preservative, is readily soluble in water, and has no smell β-naphthol, $C_{10}H_7OH$, has no smell, and is a more powerful antiseptic than phenol

Fluorides.—Sodium fluoride, NaF, sodium bifluoride, NaF.HF, and sodium silicofluoride, Na_2SiF_6, are all used as preservatives. They are colourless compounds sparingly soluble in water. In the presence of salts of calcium or magnesium, which would generally be present in dressing mixtures, they become

changed into insoluble calcium and magnesium fluorides which have no preserving action.

Zinc chloride, $ZnCl_2$, is used very commonly in sizing mixtures as an antiseptic It acts also as a deliquescent agent and, since it lowers the gelatinisation temperature of starch, assists in the preparation of the dressing mixture. It is made by burning zinc in an atmosphere of chlorine or by dissolving its oxide or carbonate in hydrochloric acid and evaporating the solution. Zinc chloride crystallises with two molecules of water, giving $ZnCl_2\,2H_2O$. Commercial zinc chloride is made by dissolving zinc in hydrochloric acid and concentrating the solution till it sets when cooled It is then cast into sticks. Since zinc chloride is hydrolysed when boiled with water, these sticks contain also basic chloride, formed thus

$$ZnCl_2+H_2O=Zn(OH)Cl+HCl.$$

Anhydrous zinc chloride may be prepared by igniting a mixture of zinc sulphate and sodium chloride, when zinc chloride distils over at 730° C. and solidifies in the receiver

Zinc chloride is a colourless substance which is very deliquescent When the solid substance is exposed to air it absorbs water rapidly and becomes changed into a pasty liquid Its affinity for water is so great that it acts as a dehydrating agent Thus it chars cellulose and other carbohydrates when heated with them. It absorbs ammonia, forming addition compounds, *e g* $ZnCl_2\,NH_3$ When in solution it forms a double chloride with ammonium chloride, $ZnCl_2\,2NH_4Cl.6H_2O$ This salt is not hydrolysed by water, and can be obtained by evaporation of its solution Concentrated solutions of zinc chloride dissolve cellulose and animal fibres, and gelatinise starch at ordinary temperatures For the latter reason it is used in the preparation of starch pastes, acting simultaneously as a preservative Owing to its property of becoming hydrolysed with the liberation of acid when heated, it is liable to cause tendering in cotton goods.

Zinc chloride is commonly bought as a concentrated solution of about 1 5 sp gr The relation between specific gravity and concentration is given in the following table —

Density at 19 5° C	Per cent $ZnCl_2$
1 645	5
1 091	10
1 137	15
1 186	20
1 238	25
1 291	30
1 352	35
1 420	40
1 488	45
1 566	50
1 650	55
1 740	60

G Smith (*J Soc. Dyers and Col*, 1921, p 25) gives the following table showing the relative efficiencies of different preservatives when used with sizing mixtures :—

	Wheat Flour	Other Starches.
	Per cent	Per cent
Zinc chloride .	8–10	6 0
Sodium silico fluoride	3 0	2 0
Boric acid	3 0	2 0
Copper sulphate	0 5	0 3
Salicylic acid	0 5	0 3
Phenol .	0 5	0 3
Sodium phenate	0 5	0 3

Tests for Zinc Chloride Solution.—When diluted with water no insoluble matter should be visible. If present it may be filtered off on a Gooch crucible and weighed. When ammonium chloride and ammonium hydroxide are added to the diluted solution no aluminium or iron hydroxide should be precipitated. If sodium sulphide be now added and the mixture warmed the zinc will be thrown down as white sulphide When this sulphide is filtered off and the filtrate boiled with ammonium oxalate, no calcium oxalate should be formed If the liquid be cooled and strong, ammonia solution and sodium phosphate added, magnesium ammonium phosphate will be precipitated if magnesium chloride be present Freedom from iron may be ascertained by treating a little of the diluted liquor with potassium ferrocyanide

The zinc may be estimated in the following way . Some of the diluted solution is treated with ammonium chloride and ammonia and any precipitate filtered off. The filtrate is made strongly acid with formic acid and a rapid stream of sulphuretted hydrogen passed through the liquid for about five minutes. This precipitates the zinc as sulphide The mixture is heated in a water-bath for half an hour to coagulate the zinc sulphide After standing for an hour or two the sulphide is filtered off on a weighed Gooch crucible, washed, ignited to zinc oxide, and weighed

Deliquescents.—The term deliquescent is used, in a general way, to denote the property of attracting moisture from the atmosphere which is possessed by some bodies But, strictly, it has only a more limited meaning, referring to compounds which become gradually liquid when exposed to moist air Calcium chloride and sodium hydroxide are examples. Many other chemical compounds attract moisture from the air, but only to a limited extent, and do not become liquid. These are termed hygroscopic. Salts containing water of crystallisation are nearly all hygroscopic Thus, white anhydrous copper sulphate, when exposed to air, combines with water to form blue copper sulphate, $CuSO_4.5H_2O$. Both deliquescents and hygroscopic bodies are used in dressings to produce a particular feel or " condition " Some of them, such as magnesium sulphate and sodium sulphate, are also weighting agents at the same time. When a deliquescent is used, the finished goods retain more moisture than they would in its absence This makes them more liable to be attacked by moulds or bacteria. Hence, an antiseptic must be included in the dressing mixture.

Calcium chloride, $CaCl_2$, occurs in sea-water and certain minerals. It is obtained also as a by-product in the manufacture of ammonia from ammonium chloride, and it may be made by treating lime with hydrochloric acid When its aqueous solution is evaporated, calcium chloride forms colourless prisms containing six molecules of water of crystallisation $CaCl_2.6H_2O$. When crystalline calcium chloride is dissolved in water, heat is absorbed and the solution

becomes colder But if anhydrous calcium chloride be dissolved, heat is evolved, owing to the formation of the crystalline salt, $CaCl_2\ 6H_2O$.

Calcium chloride is extremely soluble in water, as may be seen from the following table --

Temperature	Calcium Chloride dissolved by 100 Parts of Water
0° C	59
50° C	126
100° C	155

When crystalline calcium chloride is heated to 260° C the whole of the water of crystallisation is expelled and the anhydrous salt is obtained This is used as a drying agent for gases and in desiccators The dehydration takes place in stages, different hydrates being formed at fixed temperatures thus

At 29·8° C	$CaCl_2\ 4H_2O$.
At 45·3° C. .	$CaCl_2.2H_2O$
At 175° C.	$CaCl_2\ H_2O$

Both anhydrous calcium chloride and its hydrates are deliquescent and, like many other deliquescent bodies, readily soluble in alcohol. Like zinc chloride, calcium chloride is able to decompose many organic compounds, taking hydrogen and oxygen from them in the proportions necessary to form water. Its aqueous solutions dissolve or liquefy starch and gelatin When a solution of calcium chloride is evaporated it is hydrolysed, but to a less extent than either zinc chloride or magnesium chloride Nevertheless, it can produce tenderness in cotton during singeing or calendering Calcium chloride, like the corresponding compounds of zinc and magnesium, forms a stable double salt with ammonium chloride of the composition $CaCl_2.2NH_4Cl\ 6H_2O$.

Magnesium chloride, $MgCl_2$, has similar properties to calcium chloride, but is much more readily hydrolysed by water When magnesium, its carbonate or oxide, is dissolved in hydrochloric acid a solution is obtained But the chloride is hydrolysed so readily by water that the pure salt cannot be obtained by evaporating its aqueous solution, magnesium oxychloride being produced—

$$MgCl_2+H_4O=Mg(OH)Cl+HCl$$

But if ammonium chloride be added to the solution, a stable double salt, $MgCl_2\ 2NH_4Cl\ 6H_2O$, is produced, which is not decomposed when the solution is evaporated When this double salt is heated, the water of crystallisation and ammonium chloride are expelled and anhydrous magnesium chloride is left Like calcium chloride, magnesium chloride forms a crystalline compound of the formula $MgCl_2.6H_2O$, and both this and the anhydrous salt are deliquescent One hundred parts of water dissolve 53 parts of magnesium chloride at 0° C, 60 at 50° C, and 73 at 100° C. Magnesium chloride is used not only as a deliquescent but, also, to assist in the gelatinisation of starches It is, however, dangerous in sizes, as goods containing it become tender when singed. It is liable to tender finished goods also. This is partly due to hydrochloric acid liberated by hydrolysis, and partly to the oxidation of this acid to chlorine by moist air—

$$4MgCl_2+2H_2O+O_2=4MgO+4HCl+2Cl_2$$

The following table (Ermen, *Materials used in Sizing*) gives the specific gravities of its solutions in water .—

Density at 24° C	Per cent $MgCl_2 6H_2O$	Per cent $MgCl_2$.	Density at 24° C.	Per cent $MgCl_2 6H_2O$	Per cent $MgCl_2$.
1 0069	2	0 936	1 1062	30	14 040
1 0138	4	1 872	1 1288	36	16 848
1·0207	6	2 808	1 1441	40	18 720
1 0276	8	3 744	1 1836	50	23 400
1 0345	10	4 680	1 2252	60	28 080
1·0698	20	9 360	1 2692	70	32 760
1 0915	26	12 168	1 3159	80	37·440

Epsom salt, or magnesium sulphate, occurs native as kieserite, $MgSO_4H_2O$. When this mineral is treated with water the magnesium sulphate gradually goes into solution, the insoluble dirt and impurities being left When the clarified solution is concentrated, small, colourless, rhombic crystals of the composition $MgSO_4 7H_2O$ are obtained Magnesium sulphate is readily soluble in water, and forms double compounds with alkaline sulphates Thus, with sodium sulphate it gives $MgSO_4Na_2SO_4H_2O$ When heated it gradually becomes opaque and crumbles to a powder, owing to the loss of water of crystallisation. At 150° C it is completely changed into $MgSO_4H_2O$ At a still higher temperature (200° C) it becomes anhydrous. The dehydrated forms have the power of attracting and combining with atmospheric moisture Thus, when goods are dressed with this body and subsequently dried, they are capable of retaining moisture or taking it up after drying, according to the temperature at which they have been dried.

Epsom salt and also Glauber salt (sodium sulphate) are used extensively as " conditioning agents " for cotton goods But they are also filling agents, thus imparting both weight and condition simultaneously.

Density of magnesium-sulphate solutions (Ermen)

Density at 15° C	Per cent $MgSO_4 7H_2O$	Per cent $MgSO_4$	Density at 15° C.	Per cent $MgSO_4 7H_2O$	Per cent $MgSO_4$
1 0206	4 097	2	1 1742	32 780	16
1 0412	8 185	4	1 1982	36 877	18
1 0623	12 292	6	1 2221	40 975	20
1 0838	16 390	8	1 2472	45 072	22
1 1053	20 487	10	1 2722	49 170	24
1 1281	24 585	12	1 2880	51 726	25
1 1508	28 682	14			

Wiltern (*J. Soc Dyers and Col.*, 1921, p. 25) states that if cloth be treated with Epsom salt, dried, and again treated with the salt, tendering occurs. It is desirable, therefore, to use one treatment only. This may be done on a starch mangle, using a solution of 20° to 40° Tw. for a light and 60° to 70° Tw. for a heavy finish. At concentrations above 70° Tw the salt crystallises out in the mangle bowls and drying cans Goods after treatment become hard when stored in a dry, and flabby in a damp, atmosphere. Zinc chloride is generally added

to prevent mildew. It is better to use the Epsom salt after calendering, as this process causes tenderness if the goods already contain it.

Glauber salt, or sodium sulphate, is found native as anhydrous sulphate, and also in combination with calcium sulphate in the form of glauberite, $Na_2SO_4CaSO_4$. It is largely prepared during the manufacture of alkali by the Leblanc process Sodium sulphate crystallises from water in the form of colourless prisms of the composition $Na_2SO_4 10H_2O$. When exposed to air they effloresce, losing nine molecules of water. The tenth is given off at 100° C. Anhydrous sodium sulphate acts on fabrics in the same way as dehydrated magnesium sulphate, but it has no filling properties Its power of attracting moisture has already been referred to in connection with water softening.

The solubility of sodium sulphate in water is peculiar, as seen from the following table :—

100 parts of water at		0° C.	dissolve	12	parts of	$Na_2SO_4 10H_2O$
,,	,,	18° C	,,	48	,,	,,
,,	,,	25° C.	,,	100	,,	,,
,,	,,	30° C.	,,	200	,,	,,
,,	,,	33° C	,,	327	,,	,,
,,	,,	50° C	,,	263	,,	,,
,,	,,	100° C	,,	238	,,	,,

When crystalline sodium sulphate is heated gently it melts in its own water of crystallisation Further heating causes some of the water of crystallisation to be given off, and a mixture of $Na_2SO_4.10H_2O$ with $Na_2SO_4H_2O$ or Na_2SO_4 is formed. If the heating be continued the whole of the water is expelled and anhydrous sodium sulphate, Na_2SO_4, is obtained It will be noted that the solubility in water is greatest at 33° C This is explained by the dissociation of $Na_2SO_4 10H_2O$ into $Na_2SO_4H_2O$ or Na_2SO_4 and water The forms containing less water of crystallisation, or none, are less soluble than the crystals $Na_2SO_4 10H_2O$

Sodium-sulphate solution shows also the phenomenon of super-saturation to a marked degree. When a solution saturated at 33° C is allowed to cool in a closed flask no crystallisation takes place, although much more sodium sulphate is present than is required to saturate the water at the lower temperature If the end of a glass rod, a particle of dirt, or a small crystal of sodium sulphate be introduced into the liquid, it solidifies immediately to a crystalline mass The action of a glass rod or dirt is supposed to be due, really, to the presence of very minute crystals of sodium sulphate—that is, the formation of the crystals is dependent, always, upon the presence of a similar crystal When sodium sulphate is added to a solution containing calcium chloride, comparatively insoluble calcium sulphate is formed. Hence these two substances should not be used together.

Sodium sulphate should be completely soluble in water Its aqueous solution should be neutral in reaction, and should give no precipitate with silver nitrate When dried at 100° C. it loses about 55·9 per cent. by weight. When 1 gramme is dissolved in water, acidified with hydrochloric acid, and precipitated with barium chloride, the barium sulphate produced should weigh 0·724 gramme Sodium sulphate should be free from iron and magnesium, or carbonates of ammonium or sodium.

Glycerin or glycerol, $C_3H_5(OH)_3$, is a trihydric alcohol. It is obtained as a by-product (p. 367) in the manufacture of soap. It is a colourless, viscous, sweet-tasting liquid, with a sp. gr. of 1·265 at 15° C It is soluble in water in all proportions. Although it does not volatilise at ordinary temperatures,

it is volatilised by steam. But till the concentration reaches 70 per cent. only traces are lost. When, however, a 70 per cent. solution is boiled, water and glycerol distil over together. Pure glycerol boils at 290° C. under atmospheric pressure, but is also decomposed It distils unchanged in a vacuum at a temperature of about 179° C. When heated gently it volatilises completely, leaving no residue, and if ignited it burns, giving rise to acrolein, C_3H_4O, among other products The smell of acrolein is very characteristic. It is produced also when glycerol is heated with a dehydrating agent, such as potassium hydrogen sulphate—

$$C_3H_8O_3=C_3H_4O+2H_2O.$$

When exposed to air glycerol takes up 50 per cent. of its weight of water. It is soluble in alcohol, but insoluble in chloroform, petroleum, ether, benzol, or carbon bisulphide It has a slight reducing action on Fehling solution. Good samples of glycerin should contain from 95 to 98 per cent. of glycerol Their strength may be determined accurately from the specific gravity of the sample at 15° C Thus

Percentage of Glycerol	Specific Gravity at 15° C
100	1 2650
99	1 2625
98	1 2600
97	1 2575
96	1 2550
95	1 2525
94	1 2499
93	1 2473
92	1 2447
91	1 2421
90	1 2395

Fireproofing Materials.—The selection of the fireproofing agent and the process adopted depend largely upon whether a temporary or permanent effect is required

A temporary fireproof dressing is imparted by treatment with a solution of a salt which, when heated, gives off non-inflammable vapour, or which fuses at a comparatively low temperature. Volatile salts, such as those of ammonium, act to a certain extent because, when the fabric is brought into contact with a flame, their vapours displace the oxygen in its immediate neighbourhood. If at the same time they leave a relatively fusible residue they are still more effective Among the bodies used in this way are—

Metallic oxides, such as tin oxide or alumina.

Compounds of ammonium, such as chloride or phosphate.

Sodium phosphate, borate, silicate, tungstate, alum, or magnesium sulphate

In many cases it is sufficient to mix the materials with the dressing mixture, but where the goods have to stand washing, the fireproof agent must, if possible, be precipitated in the fibre by means of double reaction before the application of the dress, which may also advantageously contain a fireproofing mixture. Thus the goods may be soaked in a solution of alum and then passed through a dilute alkaline bath; or alternate baths of alum or magnesium sulphate and sodium

phosphate may be used. The fixing of the reagents is assisted by steaming, but many of the processes are covered by patents.

The following are the more important characteristics of some of the chemicals employed :—

Tin oxide, SnO_2, is a white powder made by treating tin with nitric acid. When metallic tin is heated with strong nitric acid, a white insoluble residue of metastannic acid, $(H_2SnO_3)_5$, is formed This is filtered off, washed, and dried, when it loses water and leaves a residue of tin oxide, SnO_2—

$$H_2SnO_3 = H_2O + SnO_2.$$

The oxide also occurs native as tin stone. When heated, tin oxide becomes yellow or brown, changing again to white when cooled It is insoluble in acids and alkalis, but when heated with solid sodium or potassium hydrate, forms $Na_2SnO_3 3H_2O$ and $K_2SnO_3 3H_2O$, known as stannates and also metastannates, $K_2SnO_3 4SnO_2 4H_2O$ and $Na_2SnO_3 4SnO_2 4H_2O$ The stannates are soluble, and hence may be used in solution, the acid being liberated on the goods by treatment with a mineral acid and converted into tin oxide by drying—

$$Na_2SnO_3 + 2HCl = 2NaCl + H_2SnO_3,$$
$$H_2SnO_3 = H_2O + SnO_2.$$

Perkin's process for the treatment of flannelette may be mentioned The material is impregnated with a solution of sodium stannate of about 45° Tw. strength, squeezed and dried It is then passed into a solution of ammonium sulphate of 15° Tw This causes the production of ammonium stannate and sodium sulphate—

$$Na_2SnO_3 + (NH_4)_2SO_4 = (NH_4)_2SnO_3 + Na_2SO_4$$

When the goods are dried the stannate is decomposed, leaving tin oxide firmly fixed in the fibre. The sodium sulphate is then removed by washing with water—

$$(NH_4)_2SnO_3 = SnO_2 + 2NH_3 + H_2O.$$

Silicates.—Insoluble silicates, such as talc, which has already been described, may be used; or soluble sodium silicate, generally known as soluble glass. It dissolves in water, and the solution, when acidified, gives a gelatinous precipitate of silicic acid, $Si(OH)_4$, which, on drying, yields silica.

Silica may be deposited on a fabric in this way. If an insoluble silicate is required, it may be produced by treating the fabric successively with solutions of sodium silicate and a soluble salt of the metal whose silicate is desired. Thus magnesium silicate may be obtained from sodium silicate and magnesium sulphate—

$$Na_2SiO_3 + MgSO_4 = MgSiO_3 + Na_2SO_4.$$

Borax, $Na_2B_4O_7 10H_2O$ (p 362), is a white, crystalline substance which is readily soluble in water. When heated it loses its water of crystallisation, and swells up, forming a porous mass.

Calcium borate, $Ca_2B_6O_{11}$, is found native. Other borates may be prepared by double decomposition by the addition of a solution of a soluble salt of a metal to one of sodium borate. Thus, if zinc sulphate be added to the solution of borax, a precipitate of zinc borate is obtained. Most of the borates have, however, a variable composition, and are generally hydrolysed by water, with the

liberation of boric acid. Fabrics treated with them must not, therefore, be subjected to prolonged washing.

Compounds of Aluminium.—The oxide, sulphate, phosphate, and the alums have all marked fireproofing properties.

Aluminium oxide (or alumina), Al_2O_3, may be obtained by igniting ammonium alum, or the hydroxide which is precipitated when ammonium hydroxide is added to a solution of an aluminium salt It is a white amorphous body which, after strong ignition, is insoluble in hydrochloric acid. In its hydrated condition it dissolves readily in acids, forming the corresponding salt of aluminium. But it is soluble also in alkalis, giving rise to salts termed aluminates. That is, it has both acid and basic properties—

$$2Al_2(OH)_6+6HCl=Al_2Cl_6+3H_2O,$$
$$Al_2(OH)_6+6NaOH=2Al(ONa)_3+3H_2O.$$

The aluminates are readily decomposed by carbon dioxide with the liberation of aluminium hydroxide—

$$2Al(ONa)_3+3CO_2+3H_2O=3Na_2CO_3+Al_2(OH)_6.$$

Ignited alumina, although insoluble in acids, may be converted into sodium aluminate by fusing it with sodium hydroxide A solution of sodium aluminate is decomposed when treated with an ammonium salt, such as ammonium chloride, the hydroxide being precipitated—

$$2Al(ONa)_3+6NH_4Cl=6NaCl+2Al(ONH_4)_3,$$
$$2Al(ONH_4)_3=Al_2(OH)_6+6NH_3.$$

Alumina may be deposited on a fibre by means of these reactions

Aluminium sulphate is found native in two forms, viz.—

$Al_2(SO_4)_318H_2O$	hair salt
$Al_2(SO_4)_33Al_2O_39H_2O$	aluminite

The normal sulphate may be made by dissolving aluminium hydroxide in sulphuric acid. It is chiefly prepared from a mineral termed bauxite by heating it with sodium carbonate in a furnace. This produces soluble sodium aluminate, the accompanying iron oxide remaining insoluble—

$$Al_2O_3+3Na_2CO_3=Al_2O_33Na_2O+3CO_2.$$

The sodium aluminate is dissolved out with water, and treated with carbon dioxide, which throws down aluminium hydroxide—

$$Al_2O_33Na_2O+3H_2O+3CO_2=3Na_2CO_3+2Al(OH)_3.$$

The aluminium hydrate is collected and washed, and then dissolved in sulphuric acid and the solution evaporated. Sodium aluminate may also be made from cryolite, Al_2F_66NaF, by boiling it with milk of lime—

$$Al_2F_66NaF+6Ca(OH)_2=6CaF_2+6H_2O+Al_2O_33Na_2O.$$

The sodium aluminate is then treated as before

The alums are double salts of aluminium sulphate and a sulphate of a monovalent metal; ammonium and potassium alums are the most important. Potassium alum is obtained in the form of octahedral crystals, when a solution containing molecular proportions of aluminium and potassium sulphate is

allowed to crystallise. Other alums are obtained in a similar manner. The alums crystallise with twenty-four molecules of water. Thus:

Potassium alum	. $Al_2(SO_4)_3\,K_2SO_4.24H_2O$,
Ammonium alum	. $Al_2(SO_4)_3(NH_4)_2SO_4.24H_2O$.

The alums are readily soluble in water. When the crystals are heated they melt in their water of crystallisation, and then, after the water has been expelled, become decomposed with the evolution of sulphur trioxide, leaving a mass of alumina and the monovalent sulphate. In the case of ammonium alum, the ammonium sulphate is also decomposed and only alumina remains—

$$Al_2(SO_4)_3\,(NH_4)_2SO_4\,24H_2O = Al_2O_3 + 4SO_3 + 2NH_3 + 25H_2O.$$

The properties of a solution of alum are exactly the same as those of one containing the constituent sulphates. Their aqueous solutions are acid to litmus paper, owing to the fact that a certain amount of hydrolysis takes place, resulting in the formation of a basic salt of aluminium—

$$Al_2(SO_4)_3 + 2H_2O \rightleftharpoons Al_2(SO_4)_2(OH)_2 + H_2SO_4.$$

These basic salts are produced also when limited quantities of alkali are added to a solution of an aluminium salt or alum, the acid radicles being successively replaced by hydroxyl groups until ultimately aluminium hydroxide is produced—

$$Al_2(SO_4)_3 + 2NaOH \rightleftharpoons Al_2(SO_4)_2(OH)_2 + Na_2SO_4,$$
$$Al_2(SO_4)_3 + 4NaOH \rightleftharpoons Al_2SO_4(OH)_4 + 2Na_2SO_4,$$
$$Al_2(SO_4)_3 + 6NaOH \rightleftharpoons Al_2(OH)_6 + 3Na_2SO_4$$

And finally with excess of sodium hydroxide—

$$Al_2(OH)_6 + 6NaOH = Al_2(ONa)_6 + 6H_2O$$

Basic salts of aluminium are less soluble in water than the normal salts. When their solutions are diluted or boiled they become more basic and consequently form a precipitate. Thus

$$Al_2(SO_4)_2(OH)_2 + 2H_2O \rightleftharpoons Al_2SO_4(OH)_4 + H_2SO_4.$$

This reaction is reversible, solution of the more basic salt taking place when the mixture is cooled. But if cotton be boiled with a solution of a basic salt much of the alumina is precipitated on the fibre. If it be then taken out of the hot bath and treated with a solution of sodium carbonate or ammonia, the aluminium is precipitated and is retained firmly by the fibre This process is used in mordanting cotton, and is available also for fireproofing purposes

Aluminium acetate, $Al_2(C_2H_3O_2)_6$, is also a useful fireproofing agent, giving at the same time a waterproof effect

Phosphates.—The chief phosphates used in fireproofing are those of ammonium, sodium, and aluminium.

Aluminium phosphate may be produced by precipitation, and has considerable value as a fireproofing agent. The cotton may be padded with a solution of aluminium sulphate, then treated with one containing sodium phosphate, and finally washed and dried. Or a cold concentrated solution of aluminium sulphate is treated with a solution of ammonium phosphate till no more precipitate is formed. A concentrated solution of ammonium chloride is then added till the precipitate is just dissolved. The goods are padded with this solution and dried

Ammonium phosphates.—There are three ammonium phosphates, viz.—

Monoammonium phosphate .	$NH_4H_2PO_4$,
Diammonium phosphate .	$(NH_4)_2HPO_4$,
Triammonium phosphate .	$(NH_4)_3PO_4$.

The most important is microcosmic salt or sodium ammonium hydrogen phosphate, $NaNH_4HPO_4$.

All these phosphates are colourless crystalline bodies, readily soluble in water. When heated they are decomposed, giving ammonia and phosphoric acid or metaphosphoric acid Thus the normal phosphate first becomes changed into diammonium phosphate, which on further heating forms metaphosphoric acid (HPO_3)—

$$(NH_4)_3PO_4=NH_3+(NH_4)_2HPO_4,$$
$$(NH_4)_2HPO_4=2NH_3+H_2O+HPO_3.$$

Microcosmic salt, when heated, yields sodium metaphosphate in accordance with the equation

$$NaNH_4HPO_4=NH_3+H_2O+NaPO_3.$$

Sodium Phosphates.—There are three sodium phosphates, viz.—

Trisodium phosphate . . .	$Na_3PO_4\,6H_2O$,
Disodium hydrogen phosphate .	$Na_2HPO_4\,12H_2O$,
Dihydrogen sodium phosphate .	$NaH_2PO_4\,H_2O$

Common sodium phosphate is disodium hydrogen phosphate. It is made by dissolving bone ash, *i e* calcium phosphate, in sulphuric or hydrochloric acid and adding a solution of sodium carbonate—

$$Ca_3(PO_4)_2+H_2SO_4=CaSO_4+Ca_2H_2(PO_4)_2,$$
$$Ca_2H_2(PO_4)_2+2Na_2CO_3=2CaCO_3+2Na_2HPO_4$$

It forms colourless crystals with the formula $Na_2HPO_4\,12H_2O$ It is readily soluble in water, its solution being alkaline to litmus. When it is neutralised with sodium hydroxide, crystals of trisodium phosphate, $Na_3PO_4\,6H_2O$, are obtained This also has an alkaline reaction. If ordinary sodium phosphate or trisodium phosphate be treated with dilute acid or carbon dioxide, it is converted into the dihydrogen phosphate, which is acid to litmus—

$$Na_3PO_4+2CO_2+2H_2O=NaH_2PO_4+2NaHCO_3,$$
$$Na_2HPO_4+H_3PO_4=2NaH_2PO_4.$$

The sodium hydrogen phosphates are converted, when heated, into either salts of metaphosphoric acid (HPO_3) or of pyrophosphoric acid ($H_4P_2O_7$). Thus.

$$NaH_2PO_4=H_2O+NaPO_3,$$
$$2Na_2HPO_4=H_2O+Na_4P_2O_7.$$

Sodium pyrophosphate is a colourless compound which dissolves readily in water and confers considerable fireproof properties upon fabrics treated with it.

Ammonium Salts.—The phosphates of ammonium have been mentioned before. In addition to these, ammonium chloride and sulphate are also used.

Ammonium chloride, NH_4Cl, is obtained by neutralising ammoniacal gas liquor with hydrochloric acid and evaporating to dryness It may also be made by heating ammonium sulphate with sodium or calcium chloride If calcium chloride be used, the reaction may be carried out in solution, the precipitated

calcium sulphate being filtered off and the ammonium chloride obtained by crystallising the filtrate. When the reaction is carried out in the dry way, the ammonium chloride volatilises and is allowed to deposit in a cooling chamber, where it forms a hard fibrous mass. Commercially the two varieties are distinguished, the former being termed muriate of ammonia and the latter sal ammoniac.

Ammonium chloride is a colourless crystalline substance with a salt-like taste. It is rather hygroscopic. It dissolves readily in water. When its aqueous solution is boiled it is hydrolysed to a slight extent, and the solution becomes acid owing to the escape of the volatile ammonia—

$$NH_4Cl+H_2O \rightleftharpoons NH_3+H_2O+HCl.$$

When the salt is heated it volatilises without melting, and if the vapour be heated strongly it dissociates into ammonia and hydrochloric acid, which recombine on cooling.

Ammonium sulphate, $(NH_4)_2SO_4$, is prepared by neutralising sulphuric acid with ammonia. Like ammonium chloride it is a readily soluble, somewhat hygroscopic colourless substance. It is also hydrolysed when boiled with water, and volatilises when heated. Owing to this dissociation, solutions of ammonium salts should be made alkaline with ammonia before drying them into cotton fabrics, or otherwise acid tendering may result. But they form double salts with magnesium which are quite stable and may be dried without decomposition, *e g.* $MgCl_2.2NH_4Cl\ 6H_2O$, or $MgSO_4(NH_4)_2SO_4.6H_2O$. These can be used without danger of liberation of acid.

Sodium Tungstate.—Tungstic acid, WO_3, is prepared by heating native calcium tungstate, $CaWO_4$, with nitric acid. It is an insoluble yellow powder, which gives rise to a number of salts known as tungstates. Sodium tungstate is prepared from it by treatment with sodium hydrate—

$$WO_3+2NaOH=Na_2WO_4+H_2O.$$

It is a whitish compound which is soluble in water, and is the most efficient of all known fireproofing agents.

Sodium tungstate is used in aqueous solution either alone or mixed with other bodies, such as borates, alum, etc.

Waterproofing Agents.—A waterproof finish is often required for cotton goods. The materials used to obtain this effect are very varied. They may be mixed with the finishing mixture, or applied separately after finishing. In the case of piece goods there are two kinds of waterproof effects, namely, (1) waterproof and airproof, and (2) waterproof but not airproof. The method used depends upon which effect is desired. With veilings and open goods only waterproofing need be considered. In the case of goods dressed with gelatin, insoluble formaldehyde gelatin may be produced either by exposure to formaldehyde vapour or by passing through a bath of diluted formalin and then drying. Casein may be used in a similar manner, or it may be rendered insoluble by a bath of dilute acetic acid. Tannate of gelatin is another substance which may be employed. To produce this, the goods are soaked successively in solutions of gelatin and tannic acid. Gelatin forms insoluble compounds with the oxides of chromium and aluminium. If alum and gelatin are incorporated with a dressing mixture a certain amount of insolubility in water is imparted to it on drying.

Insoluble soaps are often made use of. Those of the metals, calcium,

magnesium, barium, zinc, and aluminium, may all be produced by double decomposition. Aluminium soap is employed largely. The fabric is soaked first in a solution soap, and then after squeezing in a bath containing alum. The reaction in the case of sodium oleate is

$$Al_2(SO_4)_3+6C_{17}H_{33}COONa=3Na_2SO_4+2Al(OOCC_{17}H_{33})_3$$

It is then dried and ironed, or heated, to melt the aluminium soap The soaps of the heavy metals are not very stable. It has been mentioned already that they are liable to become discoloured on exposure to air They are not, therefore, very suitable for white goods The soaps of carnaubic acid, $C_{24}H_{48}O_2$, are the most stable and have excellent waterproofing properties. The zinc soap may be used.

This soap and many other zinc soaps are soluble in benzene, and may be applied as a dressing in the form of a solution

Paraffin, or other waxes, may be applied to the surface of a dressing during calendering, or as a solution in a volatile solvent which is subsequently driven off by heat. Montan wax has great waterproofing properties

Solutions of various other bodies in volatile organic solvents may also be employed Among these are shellac, cellulose acetate, and rubber. Cellulose tetra-acetate dissolved in acetone or tetrachlorethane has excellent waterproofing properties.

Oxidised oils are suitable in some cases If a cotton fabric be impregnated with a drying oil, such as linseed oil, poppy-seed oil, or tung oil, and exposed to warm air for some time, a perfectly waterproof, resinous film is formed, which is also pliable

Cellulose products, such as cuprammonium solution or viscose, are applicable for the production of limited waterproofing effects. The fabric may be padded with a solution of cellulose in an ammoniacal solution of copper oxide. The excess of ammonia is then removed by diminished pressure and passed into sulphuric acid. The fabric is then treated in a bath of dilute acid to dissolve the copper oxide, washed with water, and dried Or the cotton may be treated with a solution of viscose and, after drying, passed into a cold bath of dilute acid or bisulphite to precipitate the hydrated cellulose, and then washed and dried

Alumina is the most useful of the waterproofing agents, since it leaves the fabric permeable to air. A basic salt is generally used, which readily precipitates aluminium oxide when dried, and aluminium acetates are the most suitable. Basic acetates of aluminium are obtained by treating a solution of aluminium acetate with less sodium carbonate or bicarbonate than is required for complete decomposition. Thus.

$$Al_2(C_2H_3O_2)_6+\ NaHCO_3=Al_2(C_2H_3O_2)_5OH+NaC_2H_3O_2+CO_2,$$
$$Al_2(C_2H_3O_2)_6+2NaHCO_3=Al_2(C_2H_3O_2)_4(OH)_2+2NaC_2H_3O_2+2CO_2,$$
$$Al_2(C_2H_3O_2)_6+3NaHCO_3=Al_2(C_2H_3O_2)_3(OH)_3+3NaC_2H_3O_2+3CO_2,$$
$$Al_2(C_2H_3O_2)_6+4NaHCO_3=Al_2(C_2H_3O_2)_2(OH)_4+4NaC_2H_3O_2+4CO_2,$$
$$Al_2(C_2H_3O_2)_6+5NaHCO_3=Al_2(C_2H_3O_2)(OH)_5+5NaC_2H_3O_2+5CO_2.$$

Solutions of basic acetates are decomposed on drying or heating, and the temperature at which this takes place decreases as the basicity increases. They are decomposed, also, by dilution with water if potassium or sodium sulphate be present. When a basic acetate is decomposed by drying, acetic acid is liberated. Thus:

$$Al_2(C_2H_3O_2)_4(OH)_2+4HOH=Al_2(OH)_6+4C_2H_4O_2.$$

On complete drying aluminium oxide, Al_2O_3, is formed—

$$Al_2(OH)_6 = Al_2O_3 + 3H_2O$$

A basic solution of aluminium acetate can be made, also, by treating a solution of aluminium sulphate with lead acetate and sodium carbonate, and in this case sodium sulphate is produced also—

$$Al_2(SO_4)_3 + Na_2CO_3 + 2Pb(C_2H_3O_2)_2 + H_2O = Al_2(C_2H_3O_2)_4(OH)_2 + 2PbSO_4 + Na_2SO_4 + CO_2$$

These solutions, containing sodium sulphate, give up practically the whole of their alumina to cotton, in an insoluble condition, when dried or when cotton is boiled in them Thus, the goods may be either impregnated and dried, or boiled for some time in the liquor

The following illustrations of the methods used are given by Polleyn (*Dressings and Finishings for Textile Fabrics*, p 195) —

1 The fabric is impregnated with a solution of a basic aluminium salt, prepared as described above, and dried

2 Lead acetate (30 parts) and aluminium sulphate (30 parts) are dissolved separately in 500 parts of water The two solutions are mixed and, after allowing the precipitated lead sulphate to settle, the clear liquor is drained off and used for impregnating the fabric, which is then dried

3 Calcium acetate may be used instead of lead acetate in Method 2

After impregnating with aluminium acetate and drying, goods are sometimes worked in a bath of soap and then dried and calendered In this way aluminium soap is produced, melted, and equally distributed throughout the fabric The waterproofing effect is increased, but the fabric tends to become airproof also The soap bath may contain also such bodies as paraffin or other waxes The following illustration of such a bath is taken from the *Textile Recorder Year Book*, 1923, p 249. After drying, the material is passed through a boiling bath of 700 litres of water containing—

15 kilo soap
8 „ stearin
8 „ paraffin
8 „ beeswax
10 „ glue
5 „ linseed oil
1 „ ammonia

After passing through this bath the material is passed immediately into a bath of aluminium acetate (2° Be), squeezed, and dried for forty-eight hours at 95° F It is then moistened slightly and calendered

The Tate electrolytic waterproofing process (*J Soc Dyers and Col*, 1922, p 22) is applicable to cotton fabrics The apparatus required (U S Pat 933861, 1909) consists of (*a*) two troughs in which sodium oleate is placed, (*b*) suitable guide and draw rollers, and (*c*) vertical electrodes The anode consists of an aluminium plate, 1 inch thick, 18 inches wide, and 5 to 6 feet long It is completely enveloped in a heavy woollen pad The cathode consists of eight graphite bars, each of which is 1½ inches thick, 2 inches wide, and the same length as the anode They are spaced ¼ of an inch apart, and their ends fit loosely between metal guides which are inclined downwards towards the anode The cloth is drawn between the electrodes, and when a seam arrives, each graphite bar, in turn, is caused to move backwards and upwards until it has passed, the bar

then falling back to its original position. By means of a spring device attached to the graphite bars, the operator can maintain a constant tension on the material, regardless of its nature and thickness The cotton goods are destarched and freed from foreign matter. They are then saturated with the sodium-oleate solution in the troughs, and pass upwards over a brass roll and then downwards between the electrodes. Aluminium acetate solution is distributed on to the material by means of ducts cut at an angle of 45° on the contact fact of each graphite segment. The angles are reversed on each alternate segment so that the aluminium acetate flows down the fabric in a zigzag path, which ensures an even distribution. Ducts are provided for drawing off the surplus liquor, thus preventing the breaking down of the insulation of the electrode supports. When starting an operation the woollen pad is first saturated with water, but no more water is necessary during any one operation. The active aluminium hydroxide formed at the anode is taken up by the pad and distributed evenly over the surface of the fabric undergoing treatment, and is probably carried into the interstices of the material owing to the fact that the aluminium hydroxide is positively charged and is attracted to the cathode The fabric next passes through a bath of running water direct to the squeezers It is then passed through a second soap bath and the operation repeated with reversed electrodes. Four treatments are necessary.

The waterproof properties of veilings are tested generally by soaking them for some time in water and noting their condition. Fabrics may be tested by the method of Dannerth (*Methods of Textile Chemistry*, p. 53)

" A sample about 2½ inches square is stretched across the mouth of an ordinary thistle tube, taking care that the sample contains no selvage, as this is generally more pervious than the fabric proper. Fasten the sample securely by means of a string around the neck of the tube so that the face of the goods will be toward the inside, *i e.* toward the water The thistle tube is filled with distilled water at 20° C , is supported by a clamp above a graduated cylinder, and the amount of water passing through in five hours and in ten hours is measured in cubic centimetres. A fabric which allows no water to pass through in ten hours is considered first class. Another point which may be observed is the time which elapses before the appearance of the first drop on the outer surface "

CHAPTER XXX

MANGLING, DRYING, AND CONDITIONING.

THE initial process in finishing of cotton piece goods is the transformation of the rope into the open width and correcting the mechanical strains which it has suffered

As previously indicated (Chapter XVI), the manipulation of the cloth in the

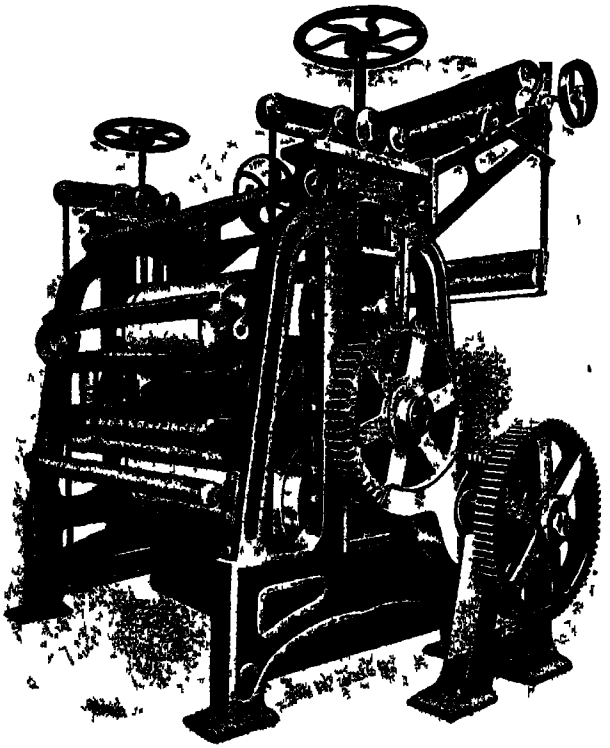


FIG. 199 —Three-bowl water mangle.

rope form terminates at the scutcher, where, by means of governed scrolls and beaters, the twists in the cloth are taken out or beaten back and the cloth is delivered in the open width It is then usually treated with a hot wash in a water mangle in the open form, to remove the last remaining traces of dirt. This process presents the first opportunity of straightening out the distortion of the weft threads acquired while in the rope form, and of recovering the width

lost in the croft. The pressure applied in this mangle imparts a degree of permanence to the recovered width

The treatment in the water mangle may be further employed according to the kind and pressure of the nips, to considerably close up the threads and smooth out the surface of the cloth, thereby assisting in the production of the

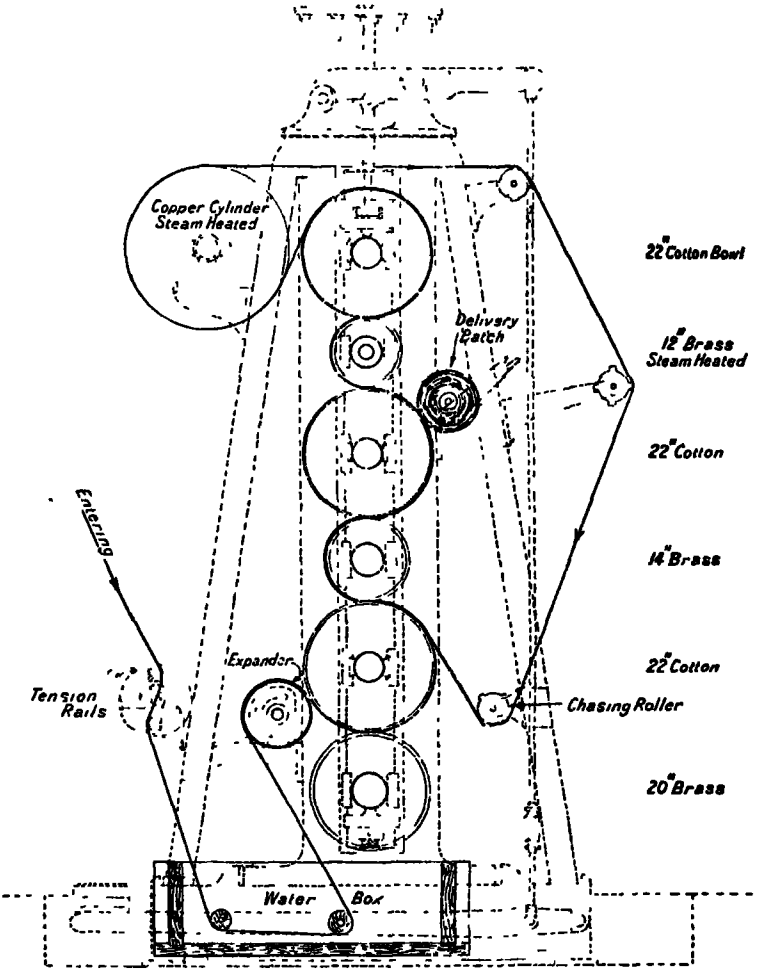


FIG 200.—Six-bowl water mangle.

required finish. The advantage of producing these effects at this early stage is that the cloth is then more capable of accommodating itself to the closing action than after a possible overdrying, which would have the effect of more or less fixing the physical structure of the fibre. On the other hand, it is possible to overdo the initial mangling of the cloth and detract from its capacity to respond to the subsequent operations by excessively reducing the resilience of the fibre. Figs. 199 and 200 respectively illustrate a three-bowl and a six-bowl water mangle, the threading up of cloth in fig. 200 being according to the procedure

known as "chasing." Although this is only one of several methods of threading up, it may be briefly referred to.

Chasing implies the re-entry of the cloth through one or more of the nips through which it has already passed, so that there are simultaneously two thicknesses or layers of cloth at such a nip, one of them passing through it for the first, and the other for the second time

The process may be further extended to effect a double or treble chase, so that in each nip in which this state occurred there would be three or four layers of cloth respectively The effect of chasing is to produce a thready appearance on the contiguous faces of the cloth. The threads on such surfaces are pressed against each other, and in a sense emboss their form on each other The tendency is to round rather than to flatten the threads, and at the same time the closing-up effect is enhanced Thus the cloth may be passed once, twice, or three times round the mangle. The last-mentioned method is mostly applied to fine shirtings requiring considerable closing and when they call for "second-time" mangling

The water mangle shown in fig 200 is often referred to as the first-time mangle; and an identical machine, but for the water box, is called the second-time mangle The cloth is run in sequence through the two machines so that it gets sufficiently dried for immediate treatment in the stiffening mangles. Owing to the smaller cost of tin drying (*i e* drying on the drying machine or "tins"), the second mangling is generally omitted, and the cloth chased through the first-time mangle to increase the closing effect, and also because after chasing the cloth presents a face more favourable to the retention of a heavy filling than if merely flattened by ordinary mangling.

The application of heat to the upper brass bowl, and the heating of the copper cylinder over which the cloth passes during chasing, swells the thread (while still damp) and enhances the subsequent closing

The mechanical features of these machines are in the main typical of a class which includes various kinds of mangles and calenders, characterised by a series of bowls, or rollers, whose centres lie in a vertical plane, and whose extensions, or necks, are supported laterally by hard brass blocks, bolted to the cheeks of the frame The pressure between the bowls, or the amount of "nip," is effected by the superior weight, including that applied through compound levers upon a thrust block usually bearing on the necks of the top bowl.

The pressure can be further increased by locking the upper lever and applying "dead set" by tightening the thrust screws which communicate between the top lever and block A suitable adjustment of pressure on each side of the bowl is obviously essential for uniform effect across the width of the cloth. The weight required on the driving side is, in practice, somewhat less than must be applied to the other, but in any case the test for correct pressure is to inspect the selvages of the cloth to see if they are equally moist. It will sometimes be found that the dark appearance accompanying relative dampness appears in streaks, say in the middle of the cloth This indicates some irregularity on the surface of the bowls, for which the remedy is scraping The surface at which the cloth bears against the bowls is liable in time to wear a depression in them, and then the outer surfaces require scraping to the common level

The degree of pressure, the composition and arrangement of the bowls, and the mode of threading up the cloth are the main factors in determining the effects produced by the mechanical treatment of cloth in machines of the roller type. This general statement must be qualified by reference to the method of driving, viz. whether the peripheral speed of the bowls be uniform or otherwise,

and also to the character and previous treatment of the cloth. The significance of these several features will be considered subsequently.

Reverting to the water mangle, whose characteristic feature is the employment of a water box, through which the cloth is run before it enters the nip, it was noted that it served incidentally to effect the recovery and partial fixture of width of the cloth.

The opening out of the width is effected by means of an expander, as described below. This apparatus is also applied to other machines, through which the cloth



FIG 201.—Scrimp rail

subsequently passes, but used in such cases to maintain the width initially gained, and counteract as far as possible the slight shrinkages that may occur at various stages.

Before reaching the expander, the cloth is first tensioned, by passing under and over wooden "stave" rails, and is then usually straightened by passing it over a scrimp rail The "scrimp rail" or "fish back" (see fig 201) is a gun-metal plate cut with sharp diverging serrations or teeth, on a curved surface, such that the cloth passing over it in a state of tension is induced to follow the

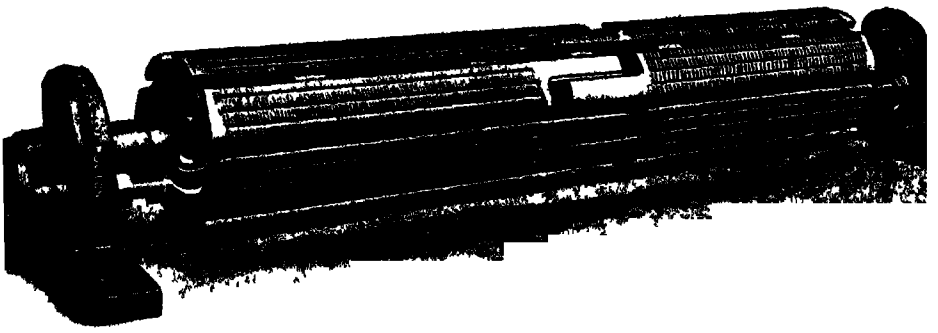


FIG 202.—Rotatory float expander

direction of the teeth These straighten out the creases, and the cloth proceeds in a straight and even condition to the expander

Scrimp rails are also made of porcelain, which is perhaps the most satisfactory material on account of its durability and cleanliness

The expander is placed as close to the nip of the bowls as its diameter will permit, so as to reduce the intervening distance in which a relapse of width may occur in the cloth. The best apparatus is a rotatory "float" expander, which is driven round by the cloth and consists, as in fig. 202, of a series of cutter rails which engage with and follow the cloth. In the period between which the cloth tangentially meets and leaves the expander, a lateral motion is continually imparted to the revolving rails, which separate outwardly, and, carrying the cloth with them, stretch or widen its face.



FIG. 203 —Finishing range.

The divergent motion of the rails is effected by their internal engagement with a stationary cam, which can be inclined to vary the degree of stretching. The interior spiders, etc., should be of brass, especially for a water mangle, and the shaft strong and rigid, but the whole as light and easy-running as possible, so as not to strain delicate cloths which may have to drive the expander. Another form of expander is shown on the mangle in fig 199, in which the diameter is smaller than that of the normal type, *i e.* 9 inches. A diameter of 9 inches is found in the case of the float expander to best combine the advantage of a large arc of contact, light weight of expander, and nearness to the nip.

The middle bowl of the smaller three-bowl mangle, also called " scutcher " mangle, which is used for lighter goods in which the closing of the threads is a secondary consideration, is made of brass, and the outer two of sycamore or cotton The sharp brass and wood nips serve to sufficiently flatten and brighten the surface of light goods

The delivery of the cloth from mangles and calenders is effected either by batching or plaiting In the batching method the end of the piece is wrapped round a wooden roller of 4 inches diameter, with a stud projecting at each end for riding on inclined arms or swinging levers so that the batch is rolled up by the frictional contact with the bowl

An alternative method of delivering cloth is by a plaiting apparatus as shown at the back of fig 199, in which the cloth is fed out through a pair of rollers, and during its descent is automatically folded backwards and forwards in laps into a wagon

The batching system economises space, but has the disadvantage of waste of time, and is very liable to cause dirt and broken ends It is the most convenient way of delivering the cloth from some machines, as, for instance, when chasing in the water mangle or calender, when the cloth emerges at a nip facing the chasing rollers But wherever possible, plaiting should be adopted for the sake of cleanliness, output, and reduction of damage and dirt For example, a wagon of cloth can be brought to a mangle, and before it is emptied the cloth in a second wagon can be joined up to it, and this continuity obviates the necessity of stopping the mangle to join up consecutive batches

Drying previous to Finishing.—After the wet mangling process, the goods are generally dried or partially dehydrated before the application of the finishing material. In some cases, however, as when a light starching is required, the stiffening is applied to the cloth immediately it leaves the water mangle or scutcher.

Fig. 203 shows a horizontal drying machine by Riley & Co of Bury. It consists of a series of steam-heated cylinders of tinned iron or sheet copper. A modern method of feeding with live steam and removing the condensed water is shown in section in fig. 204, as applied by Sir James Farmer & Sons, Ltd., to an ordinary 22-inch cylinder The cloth is fed to the machine through tension and scrimp rails to keep it straight, or an expander is sometimes employed for this purpose, and also to counterbalance any loss of width in drying (see fig. 203). It is then threaded under and over consecutive cylinders, and delivered at the other end through a plaiting machine, or rolled into batches on a drum.

Twenty-three cylinders form a convenient number for general work. Where space is limited, the cylinders are arranged in two vertical tiers connected by a short horizontal range at the top (fig. 205). One range of cylinders may be replaced by winces when it is desirable to apply the heat to only one face of the cloth. This, for example, would occur when only one side had been starched, or a pattern had to be raised.

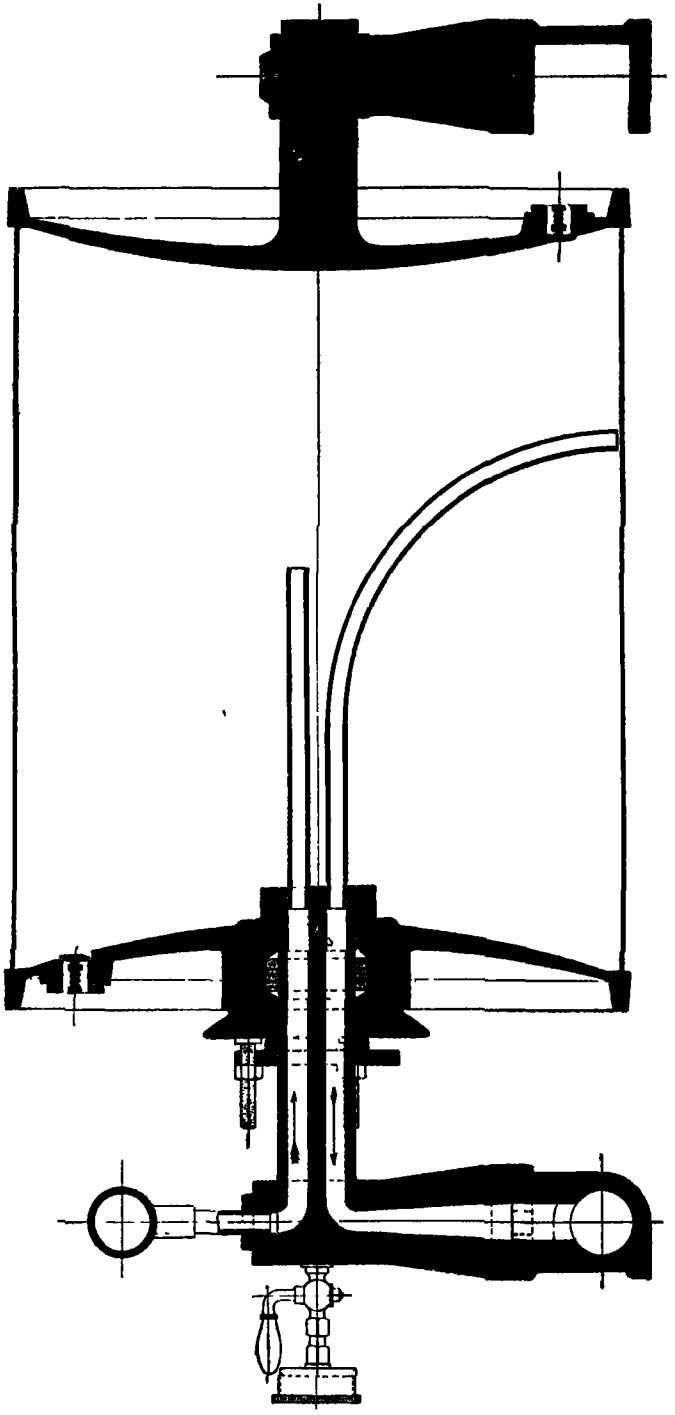


FIG 204.—Farmer's improved cylinder drying machine


J.H. RILEY & CALDBURY
J.H. RILEY & CALDBURY

This effect is, however, more frequently produced by passing the cloth over the cavity cylinder described below. This allows longer contact with the heated surface, and thus also greater swelling of the pattern threads on the unheated side. This swelling action is equivalent to steaming, and is sometimes replaced by the use of direct steam delivered from a suitable perforated pipe at the entry end of a clip stretcher.

All drying cylinders are provided with an automatic air inlet valve to prevent the formation of a vacuum by condensation of steam when the machine is stopped, or when the steam is first admitted Absence of water in the cylinders should

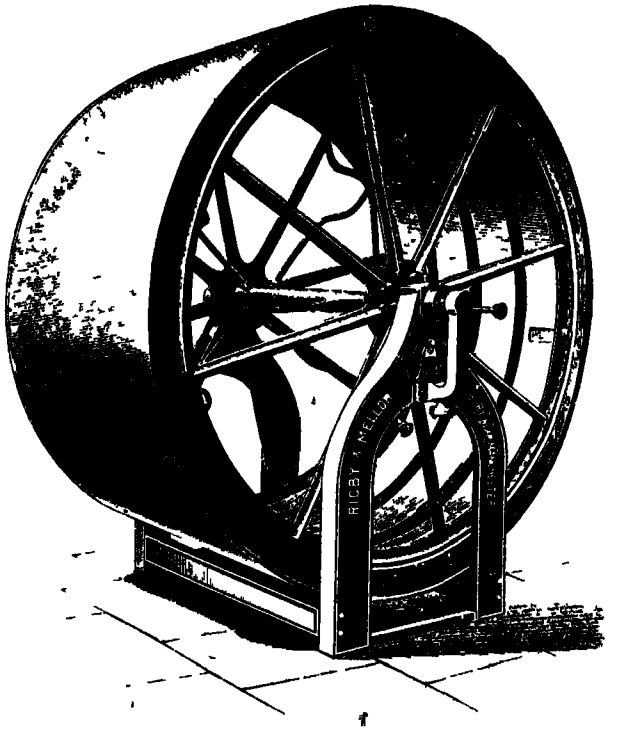


Fig. 206 Cavity cylinder

be ensured by revolving them before the entry of steam. When the steam pressure reaches the maximum for which the cylinder is designed it is blown off by a safety-valve

The drying machine is frequently employed in conjunction with a starch mangle, as in fig 203, or with the interposition of a clip stretcher, or weft straightening and stretching machine so as to form part of a continuous finishing range. A special case is that of drying the cloth coming direct from a back filling mangle As the cloth leaves the machine the adhesion of the starch may be such that it will not at once withstand the mechanical contact with the heated surface or a wince, or it would be pressed through to the wrong side of the cloth, or plucked off on to the face of the cylinders. A slight preliminary heating is then applied in the intermediate stretching machine by means of steam coils, which cause a draught of hot air to rise through the

cloth. An alternative is to increase the diameter of the first, or first three drying cylinders.

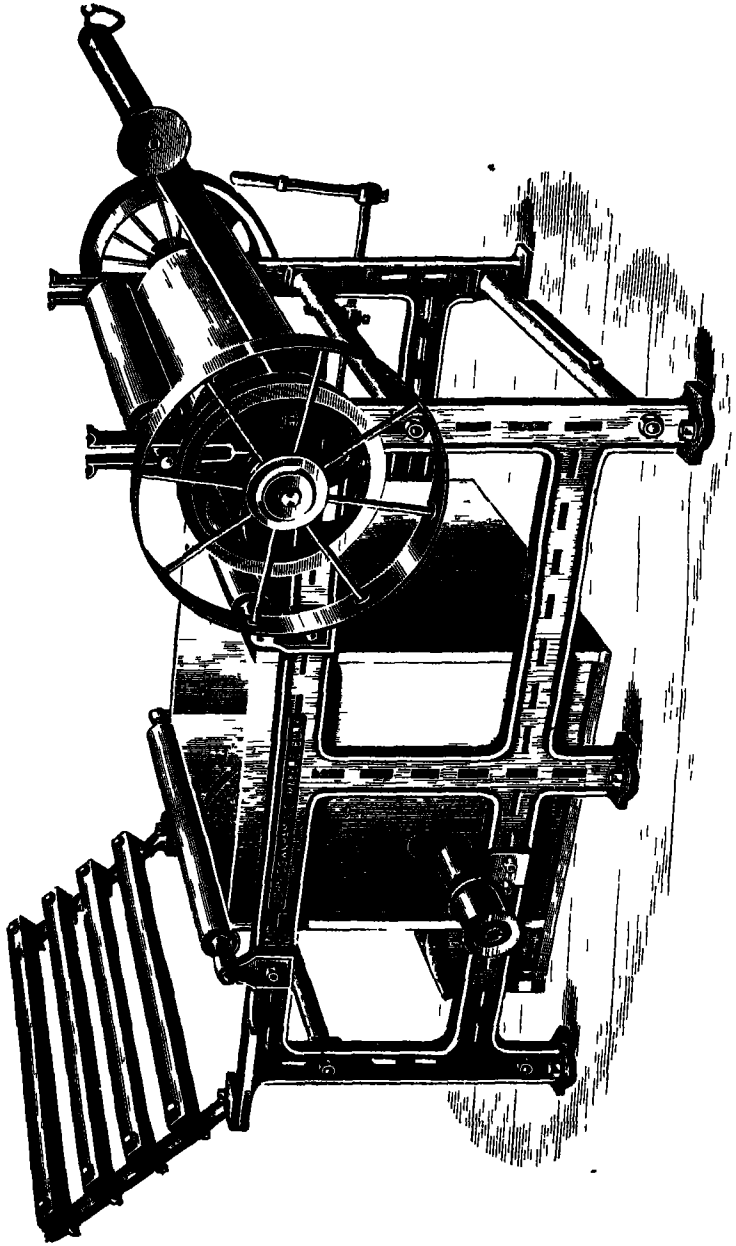


FIG 207.—Damping and conditioning machine

An exceptional case is the drying of cloth as it passes from the skimming or back starching mangle (Chapter XXXI.), and used especially for starching

thickly one side only of low cloth. The temporary difficulty of retaining the liquid paste intact until dried is met by making the size of the first cylinder 14 to 16 feet diameter, as shown in Rigby & Mellor's cavity cylinder (fig. 206), so that the starch is sufficiently firm by the time it has gone round this cylinder to stand the subsequent manipulation. Other methods of drying are by means of stoving in hot air, but this is practically superseded by the methods subsequently described in the section on stentering.

The "condition" or degree of moisture left in the cloth has an important effect on the subsequent processes, as also has the temperature of the cloth Thus in beetling and calendering a moderate degree of moisture, without heat, is conducive to a soft finish, but the same amount in cloth that has not yet cooled down would cause a harder finish. Considering the question of condition apart from temperature, a slight conditioning is favourable to a soft finish and an increased amount to a harder finish, but if the amount of moisture be excessive, and the cloth "drowned," the finish is spoilt. A degree of moisture must usually be introduced before stretching, to increase the strength or elasticity of the cloth The effect of complete drying is to render the cloth inelastic and to harden the fibre It is also obvious that the drying of the starches and other filling materials loading and clogging the fibres must necessarily enhance their stiffening effect, and this frequently calls for modification known as "breaking down" (Chapter XXXII). On the other hand, the effect of damping before drying is to raise or swell the threads In view of the significance to the finisher of "condition" and the fixation of the fibre and filling by drying, it is necessary to apply considerable judgment as to the degree of drying effected

Some finishers prefer to dry up completely, and reintroduce a definite quantity of water by means of a spray, delivered by a damping machine, since the proportion of moisture present in the cloth is thereby controlled in a more determinate manner While admitting this advantage, others prefer to condition at the drying machine, and consider that when once fully dried up, the cloth has lost something of its nature, which cannot be recovered by subsequent damping, and further, that the artificial damping is too superficial in its action

Fig 207 illustrates a damping machine by John Downham & Co , in which a spray is produced by the rapid rotation of a fine bristle roller which dips in water and throws off the drops tangentially in a fine spray or mist. The feed of water, and therefore the discharge of spray, is regulated by adjusting the height of the overflow funnel which controls the level of water in contact with the brush. The admission of the spray to the cloth, which passes over the adjustable orifice of the spray box, is regulated by varying the width of this orifice Thus, if the level of water in the box and the rate of passage of cloth be maintained constant, the amount of condition applied to the cloth is a definite quantity, proportional to and described as the number of "inches" (of width) of opening between the lids of the spray box

A modified form of spraying mechanism by Messrs Samuel Walsh & Son is shown in fig. 208, in which the spray or mist is formed by projecting fine jets of water under pressure against an inclined plate, by which they are broken up into a fine mist and applied to the face of the cloth in view of the operator, so that he can immediately detect any variation in damping. The intensity of the spray is regulated by varying the water pressure, and this is indicated by a gauge.

The temperature of the cloth is a factor of some importance. Thus, if the

cloth is still hot when conditioned, allowance must be made for its increased capacity of absorbing or evaporating the added moisture. To avoid any uncertainty thus arising, it is usual to cool the cloth after drying. Such cooling

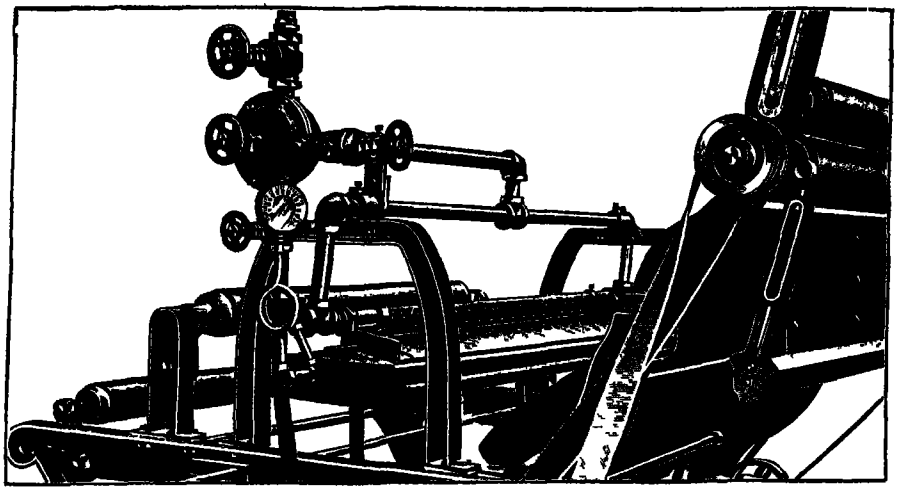


FIG 208 Dewing machine

is assisted by utilising, say, the last two cylinders of the drying machine for this purpose, and cooling these internally with a stream of water.

A jet of compressed air is sometimes employed, but the usual method is to place the wagons on which the cloth is plaited in a well-ventilated room for a suitable period to allow them to assume their normal temperature and condition.

CHAPTER XXXI

STIFFENING.

Stiffening.—The term stiffening includes the preparation and application to the cloth of various compounds which are employed either to weight the goods or partially determine the nature of their finish The formula used in mixing the ingredients and the product of mixing is termed "making," while the sequence of the processes employed in finishing is denoted by the term 'running" The "finish" is the result of the suitable application of making and running to the cloth

Any given making may be used to produce varying effects according to the method of application and the runnings employed Thus the inherent properties of a making can be, to a certain extent, developed or inhibited There is considerable scope for devising the most favourable constitution and proportions of a making to meet special conditions when the problem is approached from a scientific standpoint

The basis of nearly all makings is a paste of one of the varieties of starch or other adhesive material already described These are either employed alone or as an agent for binding weighting materials which have themselves no adhesive power Undue stiffeners are often balanced by the introduction of a softening agent Conditioning agents and other bodies having special properties are also introduced The character and functions of many of these have already been described

Preparation of the Mixture.—The stiffening mixture is made in an oak tub of about 50 gallons capacity and lined with copper at the bottom and round the rim in order to minimise wear and tear caused by stirring These tubs are generally sunk somewhat into the ground, on account of vibration, and communicate with a drain The tub is provided with a copper steam pipe which discharges at the bottom through a horizontal spreading nozzle The volume of water in the tub is generally measured by means of a graduated stick Sufficient water is placed in the tub to make together with the condensed steam and the water introduced with the starch the required volume The starch is then weighed out, made into a cream with the water, and passed through a sieve into the tub The contents of the tub are gradually heated up by means of steam, and the other ingredients are then added with constant stirring The heavier constituents, such as china clay, are added last The mixture is now gradually heated with stirring till the gelatinising temperature of the starch is reached. At this point the granules gradually become ruptured, liberating the starch, which forms a paste with the water The soluble ingredients of the mixture go into solution, but the insoluble remain in suspension, and very thorough mixing is therefore necessary to ensure the production of a perfectly homogeneous mixture If a thick paste is required, the steam is turned on full for a short time to ensure thorough agitation and gelatinisation of the mixture,

the tub being meanwhile covered to prevent splashing After thorough mixing has been effected, the steam is gradually turned off and the mixture is ready for use.

If the consistency is too high, the passage of steam is continued until a sufficient degree of "thinness" is obtained The mixing is then conveyed to the finishing machines by means of small box wagons or large cans

Accessories appertaining to the starch mixing department are a mill for grinding the china-clay or other filling material and reducing it to a paste, drum sieves with fine copper mesh, a balance, and various graduated measures for water and other liquids The practice of measuring solid materials by volume, though necessarily rather inaccurate, is largely made use of

Clay Mill—This consists of a series of rotating blades in a box into which steam and water can be passed The revolving blades break up the lumps, and sufficient water is admitted to produce an even paste This passes from the bottom of the box into a hinged oscillating sieve similar to that used in the manufacture of starch This retains any lumps, which are returned to the mill After passing through the sieve, the mixture drops into a small pit, and is ready for use Any form of mortar or mixing mill may be employed which will reduce the clay to a fine and uniform paste, in which form it is used in the preparation of the finishing mixture All solid insoluble materials should be treated in this way

Application of the Stiffening Mixture to the Cloth. The mixture is now transferred to the box of a specialised mangle, and may be applied either warm or cold, according to the density of filling required The goods are, in general, run straight through the nip, and the lower bowl gathers up and applies the starch The function of the nip is to ensure the even and quantitatively equal distribution of the paste as well as to produce certain mechanical effects The starch box may advantageously be provided with a mechanical agitator to maintain the regularity of the mixture, but this is less important with thin mixings

There are many varieties of mangles, the choice depending to a large extent on the type of finish required They may be classified as follows –

1 *Simple Stiffening Mangles*—These have mostly two bowls The most prominent example of these is the two wood mangle, which is suitable for a great variety of finishes which require straightforward starching

2 *Friction Mangles*—These are two or three bowled, and are used for goods requiring (1) heavy filling, (2) a thin smooth starchy back

3 *Back filling Mangles*—These are used for either light or heavy filling, when only one face of the cloth has to be dressed

4 *Back-starching or Slimming Mangles*—These are used for goods requiring a clean thick or thin starchy back, and are specially used for facing very low goods which mangles working under pressure would fill instead of face

The simple stiffening mangles vary chiefly in the kind of bowls employed, and whether the operation be that of a single or double nip A typical form is shown in fig 209, made by Messrs Whitehead & Poole In this both bowls are of wood The lower dips into the starch box, the latter also containing a guide roller round which the cloth is sometimes passed through the starch on its way to the nip The chief object of the nip is to quantitatively control and equalise the distribution of the starch by squeezing out excess In the case of thick finishes it also serves to impress the mixture into the fabric, but with thin finishes sufficient impregnation occurs in the starch box itself

The two-wood mangle serves for many ordinary stiffened finishes and rough finishes which are subsequently only dried and stretched It is also used to

stiffen before stentering. For this purpose the upper bowl may be tightly and evenly covered with a fent. This obviates the frequent skimming of the bowl which is otherwise necessary

For stenter work, however, a small metal bowl with brass shell is usually employed (fig 210) This acts in a manner similar to light calendering, which is also frequently applied before the stiffening A similar bowl is sometimes inserted between the two wooden ones when stiffening shirtings (see fig 203). The keener nip favours light accurate starching The second nip straightens and

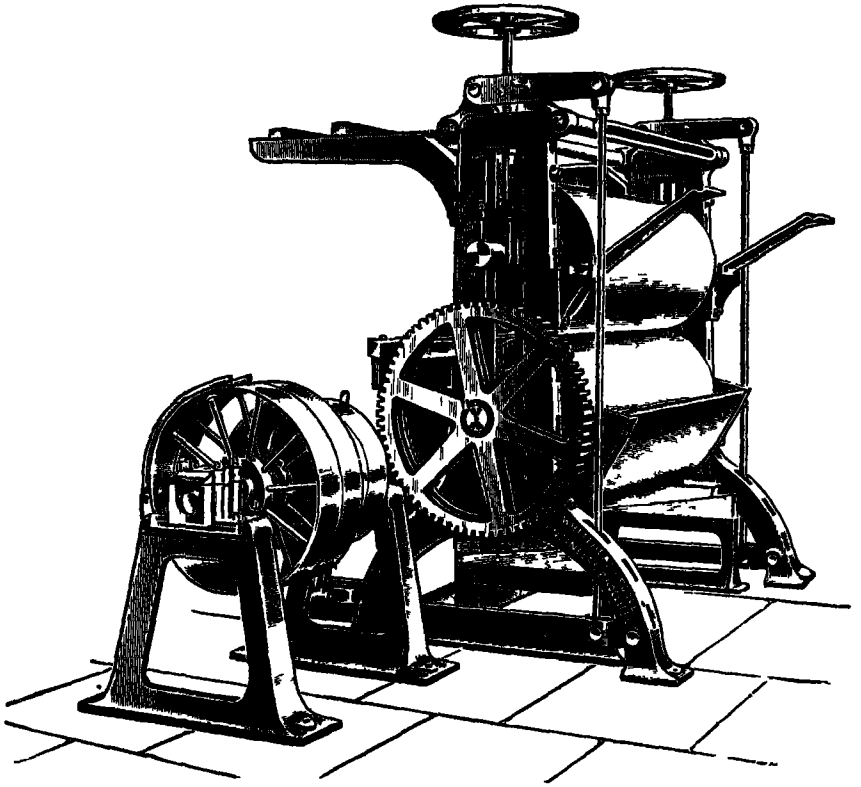


Fig 209.—Two bowl starch mangle

smooths the face of the cloth. This bowl is frequently placed above the wooden ones and can be raised out of action at will for heavier starching

The limit to the use of simple mangles corresponds with such heaviness of stiffening as leaves a smeared face on the cloth The finisher then has to make use of repeated starchings or other methods, such as back filling

In connection with wood-bowl mangles, Jardine's dipping machine may be mentioned. It is used for the dressing of isolated pieces of lace goods preparatory to drying on the frame described later. The fabrics are dipped or passed through the mixture and the excess squeezed out by means of the simple mangle. Although the method is slow, it is sufficiently rapid to keep pace with the requirements of the frames.

Friction Mangles.—The Scotch mangle is employed for very heavily filling cloth with the maximum possible quantity of stuff, to which end the cloth may be passed several times through the machine. It consists of a lower wooden

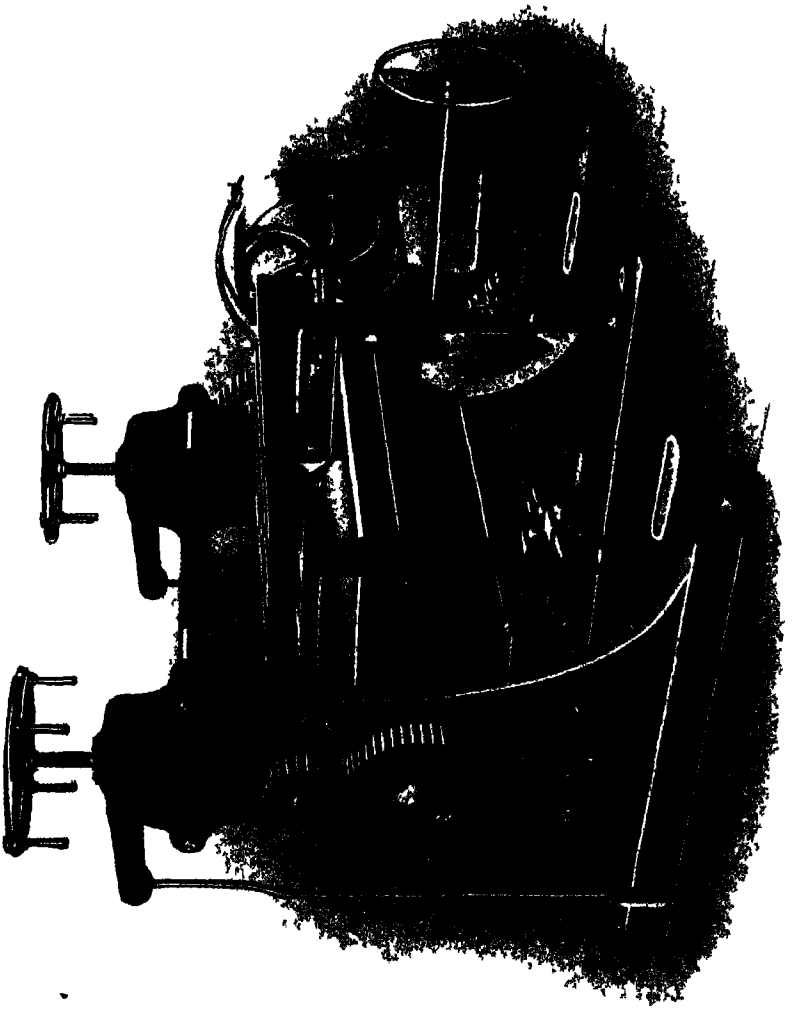


FIG. 210.—Two-bowl stiffening mangle.

bowl which gathers up the heavy mixing, and a small upper brass bowl which is geared to run at considerably faster peripheral speed. A flannel doctor keeps the brass bowl clean. The increased speed of revolution of the small bowl draws into the nip and grinds into the cloth a greater quantity of filling from the

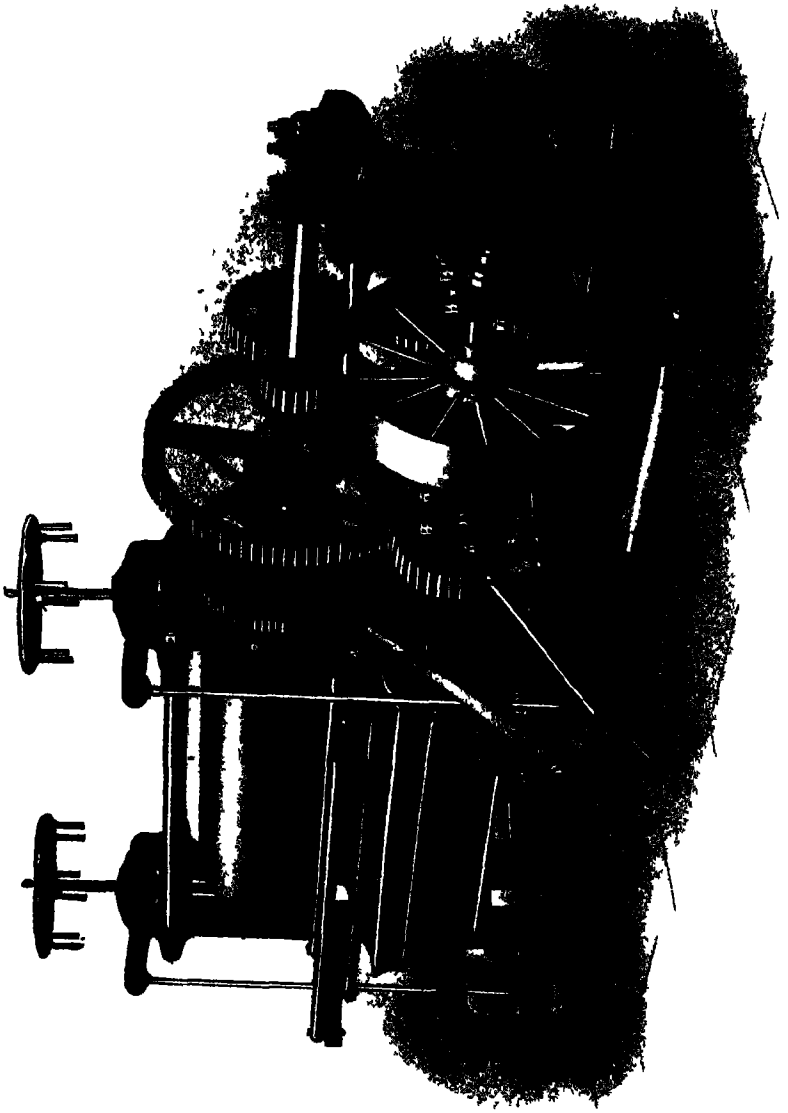


Fig 211.—Friction mangle.

accumulation of starch at the entry to the nip than would occur at a lower speed. The rate of passage of cloth corresponds with the speed of the larger bowl.

The machine is chiefly used for filling collar cloths, book backs and such-like composite productions, emery and label cloths, etc., and the process is generally followed by drying and heavy calendering

The ordinary friction mangle (fig. 211, illustrating one of Edmeston's) has a cotton lower bowl and sycamore upper bowl, these being of equal diameter.

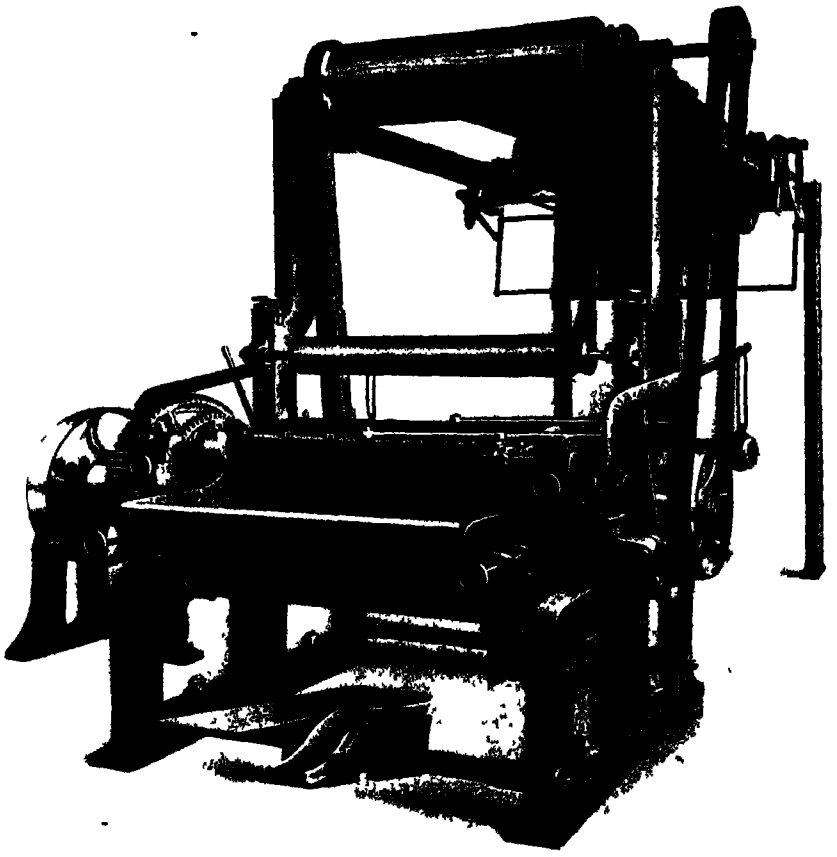


Fig 212.—Edmeston's back-filling mangle.

The cloth travels at the peripheral speed of the wooden bowl, which is slightly greater than that of the other. The cotton bowl serves the starch from the starch box, and the friction on the lower surface of the cloth causes the filling to be firmly attached, but gives it a very nice light smooth back.

Back-filling Mangles.—Messrs Edmeston & Sons' back-filling machine is shown in figs 212 and 213. In this machine the cloth may be passed through the starch box with one face closely applied to the bowl, so that it is only starched on one side. A revolving agitator maintains the regular application of starch to the exposed face of the cloth. A rubber scraper, or doctor, is mounted on the hinged shear (R) and scrapes the surface of the bowl so that it always presents

a clean surface to the incoming cloth. On the opposite side a similar metal doctor removes excess of starch from the back of the cloth and ensures the uniform distribution of the filling. Its quantitative control is by adjustment of the weight on the doctor levers and the inclination of the doctor. The manipulation of this mangle requires some care. In addition to the adjustment effected by variation of the weight and inclination of the metal doctor, its edge must be kept perfectly parallel with that of the bowl Care must also be taken to see that no grit is allowed to lodge between the doctor and the bowl If small lumps of clay or mineral be allowed to come between them, both are damaged. This trouble, however, need not occur if the mixing has been carefully made A brass shell bowl is sometimes used in preference to a sycamore bowl to improve the regularity of the work, and, if kept free from grit marks, this is a good arrangement

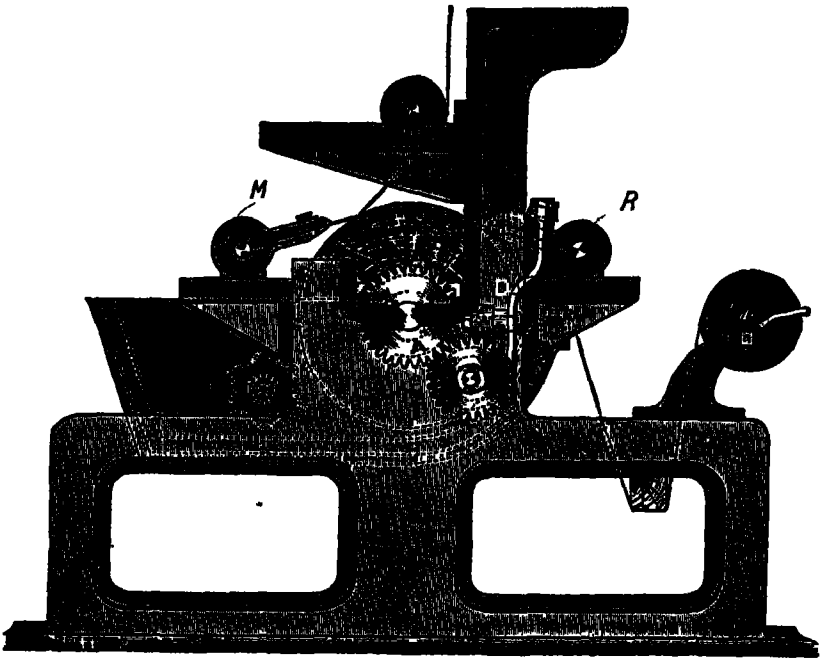


FIG 213 —Edmeston's back-filling mangle (side view)

Skimming or Back Starching.—In this method the starch is pasted on to the lower face of the cloth as it passes horizontally through the machine. A back-starching mangle is shown in fig. 214. The cloth is tensioned and scrimped and then passed under guide rollers, between which and underneath the cloth is the starch box containing two brass starching rollers, a starch agitator, and one or more doctors, all of which parts are relatively adjustable. The larger roller gathers up and applies the starch, and the smaller acts as a doctor to it, and regulates and equalises the feed of starch according to their space apart. The adjustment between the cloth and roller is controlled by elevating or lowering a guiding rail. The doctors tend to produce the equal and smooth distribution of the starch, scrape off excess, and press the starch more or less into the fabric The machine is used either in direct connection with a large cavity cylinder or a range of cylinders, according to the character

of the starching required. The cloth is threaded over guide wines to effect the largest possible area of contact with the heating surface, the starched surface being away from the metal

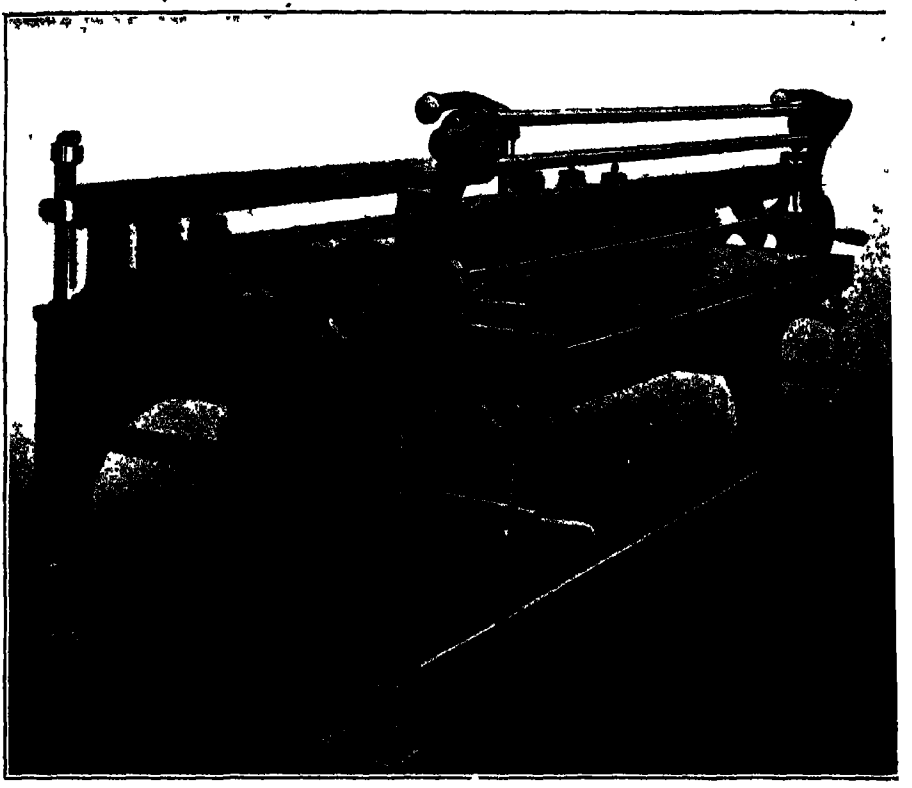


Fig. 214.—Back starching machine

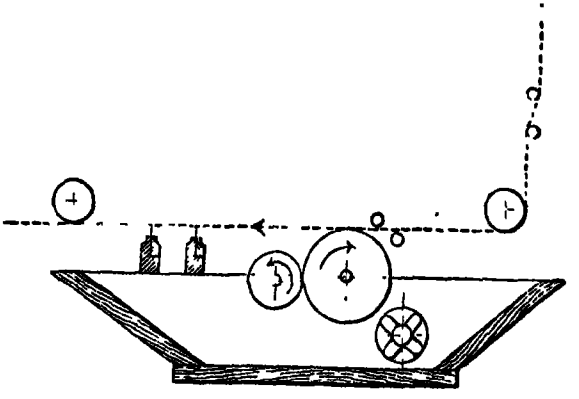


Fig. 215.—Back-starching mangle.

In all starch mangles the accurate application of starch is greatly influenced by the hardness and smoothness of the bowls, but the harder the surface the more serious are the defects caused by wear, and the greater becomes the necessity for frequent overhauling. All grit in the starch mixture must be avoided in this as in every stage of finishing The prevention of creases during stiffening is also important This is avoided by tensioning and straightening the incoming cloth by means of staves and a scrimp rail.

Where wooden bowls are used, it is important to keep them damp when not in use, to prevent cracking or warping After standing for any length of time

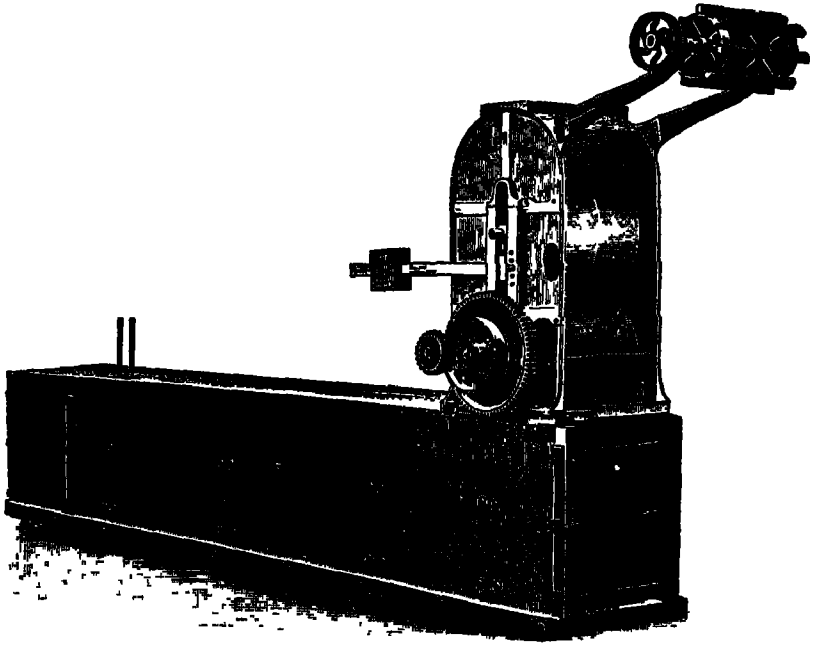


Fig. 216.—Warp sizing machine.

the bowls are run for some time before using the machine to get them into condition Irregularities of surface due to wear and tear must be at once removed by skimming up and sand-papering A bowl may be most accurately tested by measuring its circumference at various points

Warps.—The sizing of warps, which comes within the province of some bleachers, may be carried out by means of the machine made by Messrs Davies & Co, and illustrated in fig. 216. It consists of a long closed box into which the size is fed and kept boiling by means of steam. The box contains a series of copper wince rollers at each end. The warp is threaded round them in such a manner that it runs longitudinally backwards and forwards through the size. The motion is produced by revolving squeeze bowls at the end of the machine. These are provided with a layer of sizing cloth to maintain the nip most suitable for removing excess of size without damaging the warp It is necessary to keep the starch hot so that it may thoroughly penetrate the threads and not bind them together.

CHAPTER XXXII.

AUXILIARY MACHINES AND PROCESSES.

Auxiliary Machines.—Certain processes, amongst which are damping, winding on, stretching, breaking down, wetting out, and facing up, do not lend themselves to ready classification

Damping has already been considered as the converse of drying or the equivalent of conditioning, and some of its uses mentioned These include the predisposition to finishing effects preparatory to beetling, calendering, stretching, and raising. A method sometimes referred to as "rack damping" is damping combined with a form of calendering

Fig 217 is a Downham rack-damping machine. The calendering part of the machine is to the front, and consists of two cotton bowls which give a soft nip to the cloth, which batches on the upper one, and sustains the rolling weight of the top wooden bowl. The cloth passes over the damper and thence through staves to the bowls. When wound up, the bearings of the batching roller are racked up and the roll unwound or removed.

The effects produced in this machine vary with the degree of moisture introduced, and are (1) mellowing or rectifying the degree of harshness which may occur in calendering, etc , (2) brightening and smoothing the face of the cloth and giving it a nice clean appearance, and taking out "water-marks" due to chasing and beetling, (3) slightly modifying the weight by conditioning the finished cloth The machine is also called a finishing frame

The *winding-on frame*, or *canroy*, is a frame with tensioning staves, rollers, and scrimp rails, and batching tackle of some description Thus a damper may be used as a canroy if the belt driving the brush be taken off The chief use of the machine is to transfer cloth from the lap to the batch form, or to inspect it during its passage in open width It may also be converted by the addition of a knife bar whose edge bears against the cloth into a machine for simultaneously producing the effect of "breaking down."

Breaking down means reducing the harshness of a finish, and is effected in a manner that is equivalent to bending or drawing a piece of starched cloth over a hard edge, or by stretching the cloth.

The arrangement of the canroy for breaking down is shown diagrammatically in fig. 218 (*a*), while (*b*) and (*c*) show other ways for batching off the drum of the canroy. The method indicated in (*c*) is the best way, because it gives the largest arc of contact for the drum to draw the cloth. The bearings of the batch roller work in vertical slides under the pressure of springs or weights, and can be raised and held with a pawl to unroll a part of the batch for detailed inspection.

As stated above, breaking down is effected by stretching, previously to which the cloth is generally slightly damped to increase its capacity to withstand the strains which occur in the process, but a distinction exists between stretching for the sake of increasing width and that for breaking down. Excessive reliance

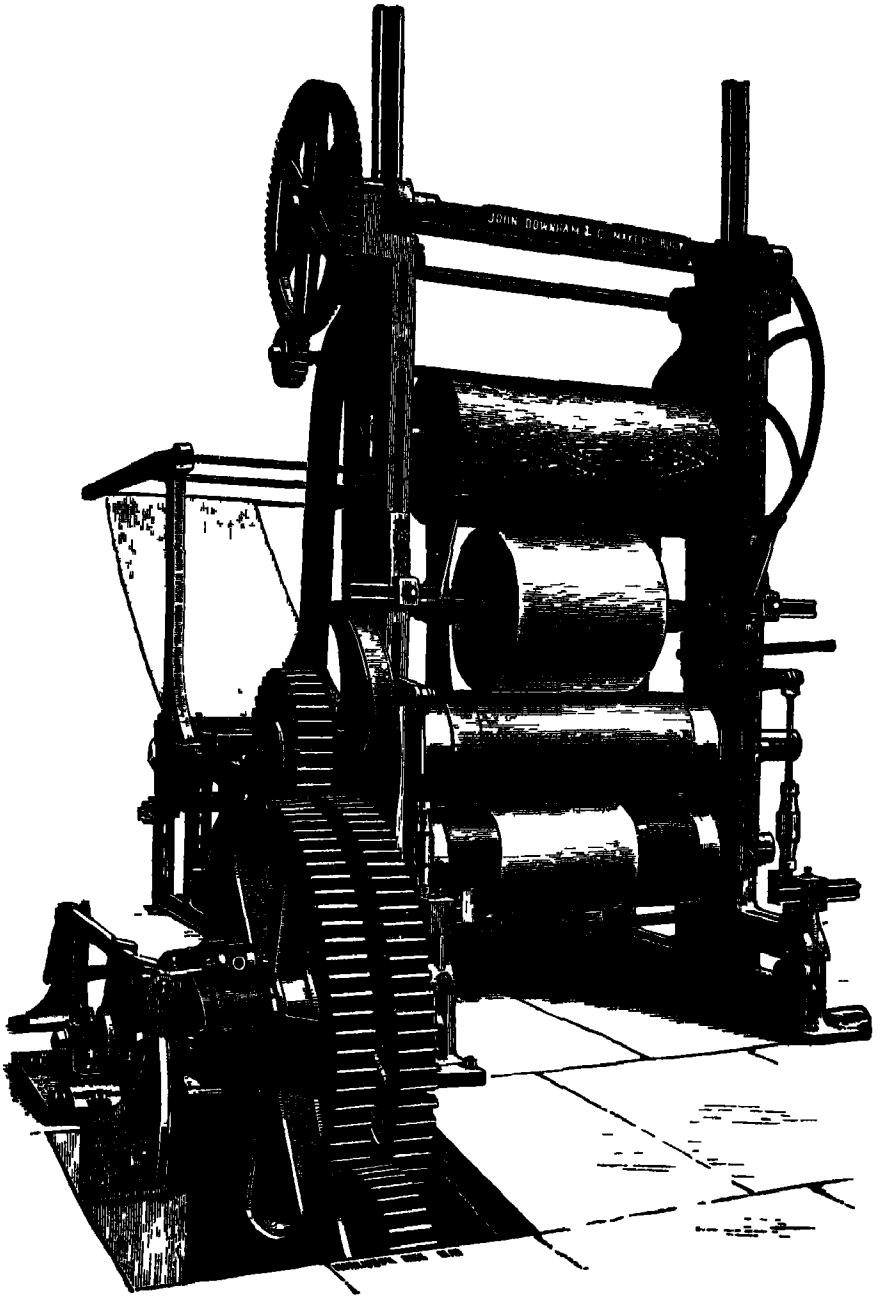


FIG. 217.—Rack-damping machine.

on this machine for the former object is to be deprecated. The required width should be obtained as far as possible from the expanders, especially in the first water mangling. Edmeston's belt stretcher (fig. 219) combines the method of drawing the cloth over a knife bar with that of stretching, and applies a means of breaking down the stiffness of the selvages, which are ordinarily left untreated because protected by the grip of the stretcher belts. This consists in passing the edges of the cloth between fluted bobbins, the result of which is to produce a corrugating effect in a longitudinal or lateral direction, which obviously increases the strain and therefore the breaking effect upon this part of the dressing.

The rest of the machine operates by gripping the selvages of the cloth against the rubber tyres of revolving wheels, whose virtual axes of revolution are inclined so that the cloth enters the grip where the rims of the wheels are relatively close, and leaves where they are further apart

The grip is effected by an endless strap which bears against the semi-

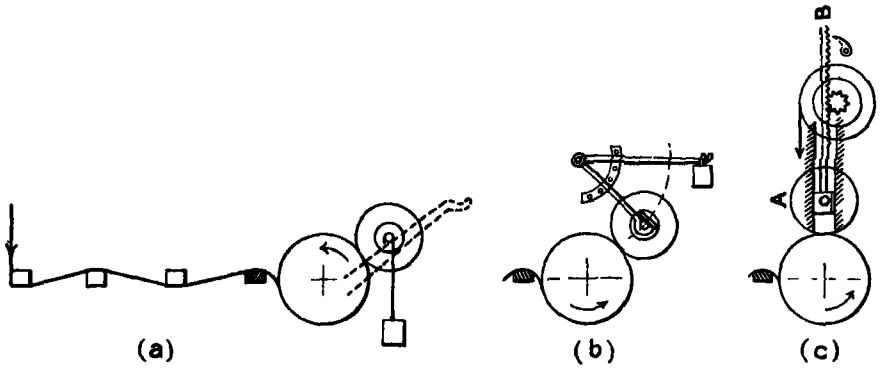


FIG. 218.—Batch winding gears.

circumference of the wheel and then returns on itself by means of jockey pulleys

The cloth is firmly held between the strap and the rubber tyre of the pulley, and when threaded into the grip effected by their conjunction must revolve with the wheel till it is liberated diametrically opposite. During this process it sustains a stretch depending on the angular divergence of the two wheels. The effect may be enhanced by the engagement with the cloth of the rims of a pair of small wheels which press against the cloth as it lies between the three internal rings shown in the figure.

The breaking-down effect due to stretching obviously follows from the tightening of the weft threads and disturbance and relative separation of the warp threads and the dressing materials incorporated with them.

The chief disadvantage of the stretcher is its liability to tear cloth that has already undergone considerable strain, and even if these have only produced local weakness, the stretcher is apt to discover such defects and suddenly produces a considerable rent. When, however, the machine is adopted for stretching purposes, allowance must be made in the hardness imparted to the goods for the breaking down that will result from the stretching, though the knife-bar effect can, of course, be omitted. If this hardness has been overdone and the stretcher fails to sufficiently soften the finish, the fault may be corrected

by wetting out in a mangle with a little softening material. One, two, or three cotton nips in a calender have a breaking-down effect.

A recent addition to the class of machinery employed in "mellowing" or "breaking" is the spiral breaking machine of Sir James Farmer & Sons, Ltd.

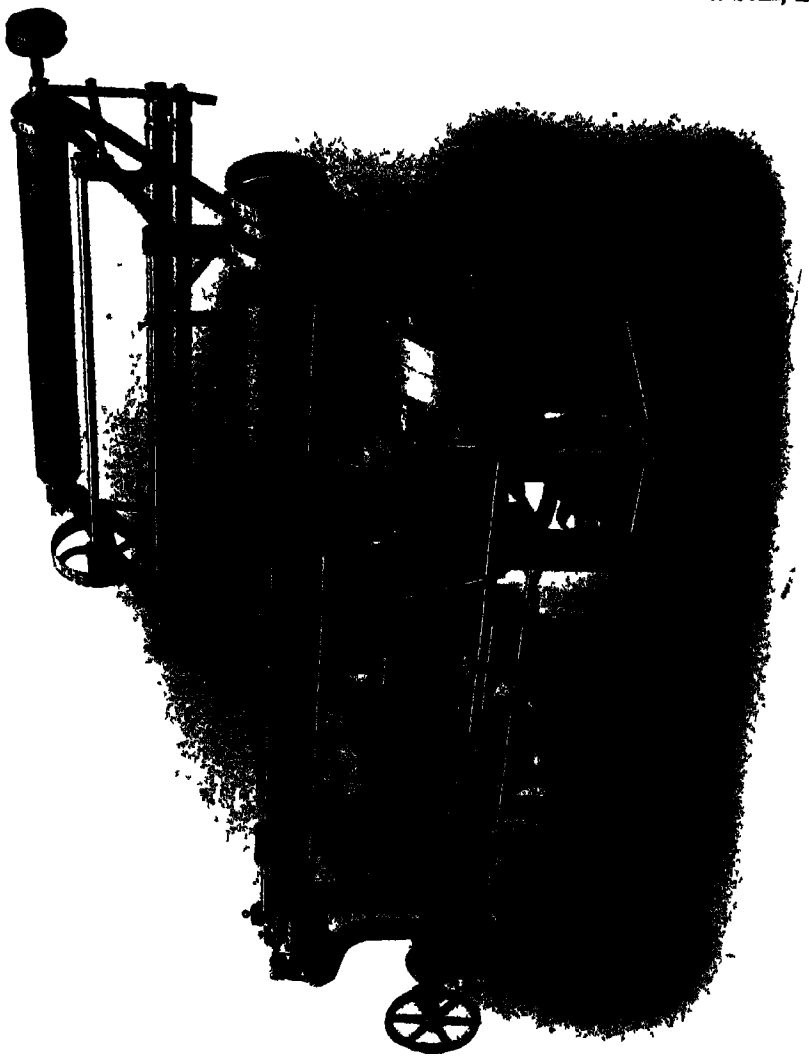


Fig 219.—Cloth-stretching machine.

It consists (fig. 220) of a number of right- and left-hand scrolls, between which the cloth is threaded in its passage through the machine towards the draw rollers. The scrolls are carried alternately in fixed and quadrant bearings, the latter being adjustable by a common handle, to impart more or less break as required.

Each of the scrolls is geared to revolve in the same direction as that of the cloth in contact with it.

A special feature is the repeated application of moderate but uniformly distributed stresses to the cloth in passing once through the machine, as contrasted with the more severe local tension and strain incidental to some of the methods described earlier.

As compared with fluted or toothed rollers, one observes here the combination by scroll action of the longitudinal and lateral deflections and the avoidance of corrugating effects in one or other direction

A reversing striking gear facilitates preliminary trials during adjustment of the required break, and a scroll adjustment indicator affords a standardising reference.

An alternative device employed in the same machine is to substitute bobbins

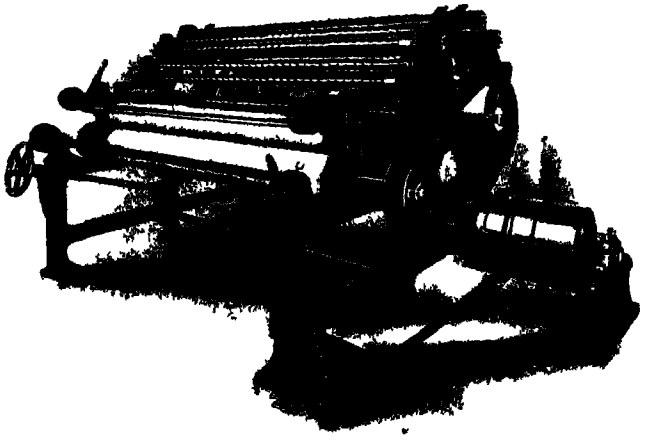


FIG 220.—Farmer's spiral breaking machine

with lateral flutings, in effect wooden cog-wheels The depth of gearing in either form is adjustable, so that a greater or less degree of distortion of the dressing may be effected.

Wetting out consists in passing the cloth through the nips of a two-bowl mangle and applying by the lower bowl a film of water or a light dressing of softening material or starch to modify the finishing effect already produced. This modification is chiefly in respect of softening, or cleaning up and smartening the face of the cloth or preparing it for a conditioning finish.

Facing up refers to finishing off the finishing frame or rack damper, but also to the application of a dressing or filling in the two-bowl mangle as, for instance, when the face of a back-filled cloth requires to be slightly or more heavily filled to complete the finish.

CHAPTER XXXIII.

STENTERS.

THE processes described in Chapters XXX. to XXXII. do not necessarily represent successive stages in the routine through which the cloth passes, as it may be treated by one or more of the processes of stentering, beetling, and calendering, or miss all of them. There is therefore no significance in the sequence adopted in this chapter.

The relation which the typical processes bear to each other is considered subsequently after their characteristics have been defined.

The process of stentering relates especially to the lighter qualities of cotton goods, particularly such as are woven somewhat loosely, and must be dressed with a view to the maintenance of their pattern undistorted, and where the effects of air-drying or absence of pressure in the starched threads is a consideration.

Stentering.—After such goods have been "dressed," they may be "stentered" in order to effect the following objects —

1. Bringing them to the desired width
2. Straightening of the weft threads and establishing the designed pattern
3. Drying of the goods by means of hot air whilst in this state
4. Producing the desired feel in the finished goods by the suitable application of heat in conjunction with, or without, special motions being applied to the cloth.

The goods are stretched upon a machine known as a stenter (fig 221) in such a way as to straighten out and produce the necessary width with a minimum of mechanical strain. They are then dried by means of hot air. In this way, the fixing of the dressing occurs while the cloth has the desired width and form. Further, by regulation of the temperature, and therefore the rate of drying, combined with a motion known as "swissing," which is given to the cloth, the nature of the final "feel" and the elasticity can be controlled This is due to the fact that the starch is in this way prevented from setting at the junctions of the threads in the same manner as if the threads remained relatively stationary

A stenter consists essentially of two extended horizontal frames provided with means of supporting and stretching the cloth between them The distance between the frames is adjustable, and the fabric is gripped close up to the selvages. Thus, in woven goods, tension may be applied directly at the ends of the weft threads, thereby providing a means of simultaneously stretching and straightening them while in the damp state

The forms of stenter to be described may be classed as—

1. Stretching and weft-straightening machines..
2. Progressive stenters.
3. Stationary clamp frames (ordinary).
4. Stationary stenters (wide).

The first named are usually called clip stretchers, and are sometimes used in place of the belt stretchers.

Fig. 222 shows such a machine, and consists of a pair of rails each supporting an endless chain of clips which open as they pass under the cam plates at the receiving and delivery ends to grip and liberate the cloth respectively. The details of clips are dealt with later.

The width between the frames can be adjusted at either end and is set to decrease towards the receiving end, thereby extending the width of the cloth which stretches across the machine between the clips on opposite frames. A modern improvement consists in regulating the speed of one of the chains during the operation of the machine, to give a drag, or lead to the selvage which is seen to be in advance of or behind the other, and thus straightening out the weft

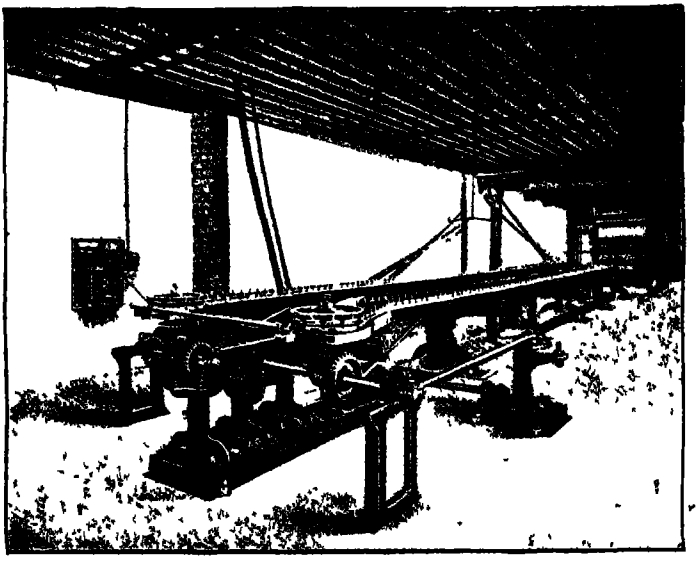


Fig. 221 —Farmer's stenter.

threads lying between them. A clip stretcher is of service as an intermediate member of a finishing range—as, for instance, between a stiffening mangle and a drying machine—treating stronger cloths than those mentioned above, as it delivers the starched material at uniform width to the drying tins Or, if the filling demands a slight preparatory drying before it can face the tins without plucking, a short intermediate stenter provided with air-heating coils may be employed

The commonest use of stenters is for the combined purposes of stretching, drying, and finishing, in continuous sequence, the lighter fabrics mentioned. The heating is effected by a blast of air, heated in a tubular heater, and driven by a volume fan through the heater and an air duct, which delivers into funnels which direct it upon the underside of the cloth. When the width of the cloth permits, most of the work is performed in progressive stenters, using the clip chain or, more rarely, a pin chain. The frames are usually 30 yards in length, and built up in a series of sections mounted on swivel blocks which slide on

swivel brackets in the manner indicated in fig. 223. The distance of the frames apart is adjusted by means of a right and left screw which engages a

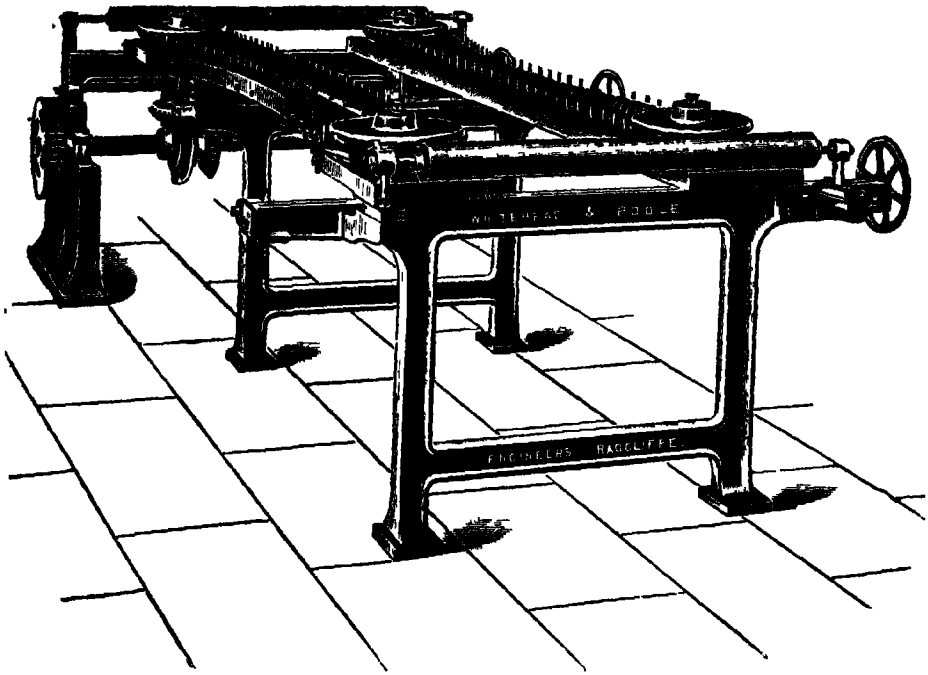


FIG. 222.—Automatic self-feeding clip stretching machine.

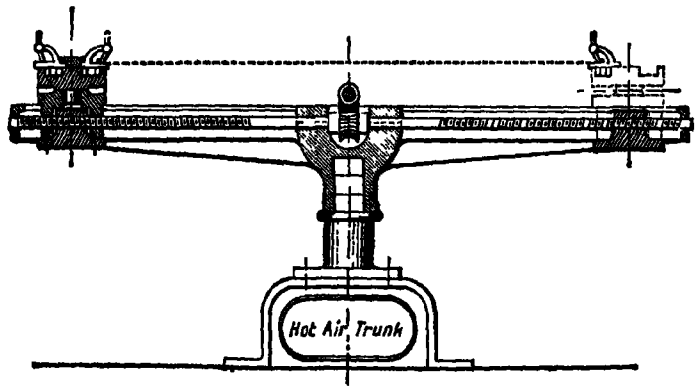


FIG 223.—Section through swivel bracket.

nut in each block, and which is itself operated by a central worm wheel, driven by a worm on a longitudinal shaft. This shaft simultaneously operates similar mechanisms in each of the swivel brackets on which the whole frame is supported. These brackets are supported, as in this case, by a pillar, which

spans the hot-air duct, and the joint between pillar and bracket permits the latter to oscillate and produce the effect known as swissing or jigging. This motion is represented diagrammatically in fig. 224, which is a skeleton plan of the framework, extending over three brackets, and showing the eccentric or jig plate, and connecting rod, which impart the oscillatory movement to the system. (For the complete machine see fig. 221.) One object of this motion which is imparted to the weft threads is to assist their straightening out whilst under tension—an action which can be readily appreciated by imitating the motion

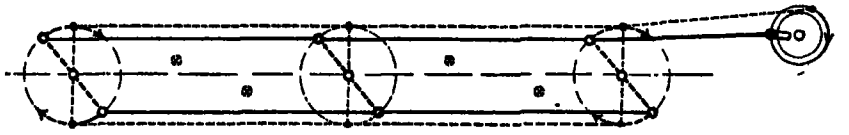


Fig. 224.—Diagram of swissing motion

by hand on a loosely woven muslin, and observing the rectification of the cross threads which occurs

If the same experiment be applied to a piece which is dressed with starch, it will be noticed that the dressing is affected. This partially illustrates another effect of swissing which alters the conditions under which the dressing is permitted to dry in contact with the material, and this affects the resultant finish of the cloth.

This so-called swissing motion is adjustable with regard to rate and extent of traverse, or may be stopped altogether; the swivel arms are then brought to the middle position, and the frame locked for straight stentering At the end of the machine where the cloth enters, the last two or three sections of the frame are so mounted on their swivel arms as to permit of their distance apart being

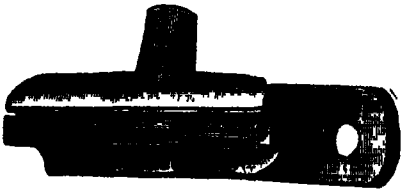


Fig. 225.—Spring-clip link

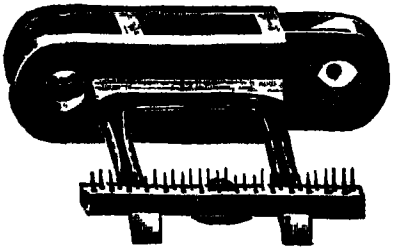


Fig. 226.—Pin-rail link.

independently adjusted to facilitate feeding. This also allows of the gradual stretching of the cloth till it reaches the normal width, at which it is dried and finished.

The delivery from the machine is by means of a plaiting tackle, the draw rollers of which are geared in synchronism with the speed of the chain, and placed at sufficient distance above the end of the machine to accommodate the swing of the cloth which occurs when swissing.

An alternative method of driving the chain is by arranging the chain wheels vertically. This is now almost obsolete, but is convenient with links forming a pin chain.

Figs. 225 and 226 respectively show spring-clip and pin links for that style of stenter. Fig. 227 illustrates a clip link as made by Messrs Mather & Platt.

The hinged upper lip is opened by the cams, as shown in fig. 221, pressing a lug on this lip forward, and when the cloth is fed under the lip and the lug leaves the cam, the lip drops. But a projection at the back of the lip and carrying a wheel rests on the cloth until the cloth has so far receded that the support of the cloth is removed from the projection. The wheel then drops into a recess in the platform behind the lower lip, and the edge of the upper lip just drops in time to catch and detain the selvage. There are many types of clip with various refinements of detail, but the above is typical, and a good one. It is most important to keep the lips parallel and well bedded, or the cloth will suffer from clip marks and curly edges through mis-clipping The usual method of attaching the material to the non-progressive frames is by means of steel pins or hooks which are mounted on the frames. The cloth is supported slightly below the level of the pins by means of cross-bearers, unaffected by the widening of the frames, and then the edges of the cloth are drawn by hand over the pins and pressed into them by means of a little revolving wheel mounted in a forked handle The frames are widened out, and the cloth so stretched is dried by hot air To remove the cloth, a rope which extends the length of the frame, and lying close to the pin rail, is tightened by means of a hand winch, so that when taut it rises above the level of the pin rail and draws the cloth off The cloth is then withdrawn endwise over a rail in a series of laps

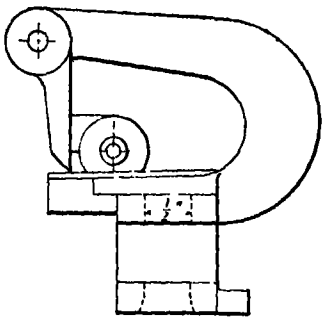


Fig 227 — Self-feeding clip link

When the width of the fabric exceeds 72 inches, as frequently occurs with lace, which is made in a great many widths, connected by draw threads, the frames are carried by wheel brackets, mounted on rails for widening out The distribution of the hot air over the cloth is effected by wafters which agitate the air rising from heating pipes, and beat it down on the face of the fabric.

Mechanical conditions favourable for good stentering are (1) A good type of clip which affords a wide opening to assist feeding, presses lightly on the cloth during engagement, and then closes sharply and grips it firmly and uniformly close to the selvage. (2) Accurate bedding of the clips in the chain race so that their lips are horizontally in line and the gaps between consecutive lips very slight. (3) The spacing of the rivets and correction for unequal wear is of the first importance, as although it would seem obvious that the cloth must proceed accurately through the stenter if it is fed in straight, and the speed of chain wheels is uniform, this does not by any means follow. If the clips are not spaced quite equally, the travel of the selvage will gain on that side at which the chain is slack. (4) An ample supply of hot air, which can be provided by a Sirocco (low pressure, high volume) fan if the passage through the heater, duct, and funnels be well proportioned. A steam-heated tubular heater with copper (Rowe) tubes gives good results. The heating surface should be such as to yield a temperature of 180° F. to a draught of 2 inches water pressure at two 4-inch outlets every 6 feet of stenter length.

The funnels should have adjustable deflecting and spreading cowls arranged to direct the draught uniformly on the cloth or check it as required for the finish.

A cloth curtain suspended from the frames to the floor prevents the access of cold-air draughts to the fabric or the escape of the hot draught excepting through the fabric.



FIG. 228.—Patent pneumatic guider and feeder

The delivery from the stenter is usually by means of plaiting tackle. A few steam-heated cylinders are sometimes used to dry off outstanding cords and selvages before the cloth reaches the plaiter, so as to avoid having to dry these off in the stenter at the expense of overheating the thinner threads in the sunk groundwork. "Condition" can, of course, be left in the cloth in stentering just as in the drying, in fact, baking the threads is always to be avoided, as it results in unnecessary harshness and risk of tearing. The heat is checked or omitted at the feeding end for the same reason.

"Splits," or goods with a double central selvage, can be parted as they leave the stenter by tearing, or cutting with a well-bevelled knife-edged tool, free to move laterally, under the control of the selvages. Tearing is effected by threading the two halves of the cloth in opposite directions over guide rollers.

The operation of feeding cloth into the stenter demands some care, especially when jigging is in operation. The desideratum is to maintain the same rate of feed at each side so that the weft lies at right angles to the selvage. The correction for a gaining selvage is to put a drag on it until the other has caught up. It is also necessary to feed the cloth sufficiently, and not too far, into the clip, especially in the case of a spring clip of the non-automatic type Rectification of lag or lead of selvage can be corrected by a modern device which admits of varying the speed of one of the chain wheels.

Fig. 228 illustrates an automatic method of feeding a clip or pin stenter, made by D. Foxwell & Son, Manchester, and it is said to be largely used by calico printers, dyers, finishers, and bleachers with extremely good results. It is equally good for open as well as closely woven goods, and the method of operation is exceedingly simple and ingenious.

It consists in directing the selvages to the clips in a manner which under suitable conditions exceeds the accuracy and speed of hand-feeding. The edge of the cloth is fed through a series of guiding rollers and winces which have the property, depending on their angular adjustment and mutual relationship (or tension), of drawing the selvage relatively into or out of engagement That is to say, the selvages can be directed to occupy a definite distance apart as they feed into the machine and clips. When a selvage reaches a certain stage of engagement or lateral extension, it touches a trigger pneumatically controlling the relative tensions of the rollers, so as to induce recession of the selvage. When this occurs the reverse action immediately supervenes, and the selvage is kept within an eighth of an inch of a definite line of travel. Space precludes more detailed description, but other refinements of adjustment, such as the method of centering the feed and accommodating the swissing motion, are developed to a practical issue.

The apparatus is of interest apart from stentering as effecting a regular feed of cloth at the desired width into any other apparatus.

CHAPTER XXXIV.

BEETLING.

In marked contrast with the methods and effects of stentering are those of the remaining processes to be described, which depend on the application of pressure to the fabric under treatment. The effects resulting from various forms of such treatment are very numerous, and are considered in connection with the several typical processes These include beetling, calendering, and stationary pressing.

The last named may, as least important, be disposed of briefly. It is a process mainly employed in the making-up room for giving a more marketable appearance to the pieces after they have been " made up " or folded and silked, taped, and so forth, as the case may be. It is also used to make them more compact for packing purposes The apparatus consists of an ordinary hydraulic press as used for baling A pressure of 2 tons per square inch on a 15-inch ram suffices for all purposes. Large pumps are desirable for expeditious work. The process is too slow for extensive use in a finishing sense, but it can be used to somewhat modify the appearance especially of the outside laps of the pieces. If it be desired to maintain or enhance the glaze, polished sheets of millboard are interposed between the successive layers of piece goods that are assembled in the press plate.

Steam-heated chests are also employed in the same way, especially in the finishing off of isolated manufactured articles, such as garments and hosiery, which cannot be finished in a continuous process. They are mounted on formers or boards to stretch them to the desired shape, and piled in the press, which may be operated mechanically or by hydraulic power

The process of **beetling** consists of subjecting the cloth to a rapid succession of blows independently and consecutively applied across its surface by a series of hammers or fallers. Each faller delivers about seventy-two blows per minute, but each successive blow strikes the surface at a different point owing to the progressive and lateral movement of the cloth. The smooth wooden face of the faller is rounded so that the contact is limited to a small area within which the more centrally disposed threads sustain a vertical pressure and the outer ones a more oblique one, tending to cause their lateral deflection. The sum of these oblique impressions constitutes what may be described as a rolling motion tending to round the threads. The vertical blows, on the other hand, cause flattening and extension, so that the total result is a combination of these effects.

There are various forms of beetling machines, such as flat beetles and roller beetles. The former produces considerable burnishing and firmness, but is rarely used. The cloth is manipulated on a flat table or rests on a sheet of glazed millboard while subjected to the blows of the fallers.

The roller beetling machine is described later. The chief effects of roller beetling are—

1. Closing up the threads of the cloth and eliminating the "pinhole" or "grinning" effect due to spaces between adjacent threads.
2. Producing a bright, hard finish, or one that is relatively dull and clothy and thick.
3. Increasing the width of the cloth
4. Leaving a surface effect, known as a water-mark.

These effects are not, of course, all produced simultaneously.

A beetling machine, as made by Messrs Arch. Edmeston & Sons, is shown in fig. 229, and consists of a row of beech fallers resting between two pairs of rolled-steel guide rails ground and glazed on their working surfaces Lateral play between the fallers is reduced to a minimum by planed distance pieces. The wiper, or compound helical cam, which raises the fallers by engagement with their projecting tappets, consists of a series of three-armed cams, mounted on a common shaft. The shape of the cam is so designed that, at the commencement of the lift, the point of contact between it and the tappet of the faller is on that part of the working surface of the wiper having the least velocity. This reduces the shock which inevitably occurs in overcoming the inertia of the faller. At the summit of its rise, the engagement between tappet and wiper arm ceases, and the faller drops by its own weight and delivers a blow to the cloth beneath. By reason of the helical mode of assembling the unit cams, the fallers drop consecutively and not in unison.

The long rollers or beams, around which the cloth is wrapped for beetling, are made very strong and stiff, and are well balanced. The arrangement for winding on is as follows :—

At one end of the beam is a spur wheel (the teeth of which are only employed for revolving the beam during the actual beetling operation), whose outer face is turned up to form a friction plate, and pressed into contact with a paper friction pulley which revolves at right angles to it. The necessary pressure to effect driving contact is applied through the end shaft of the beam by means of thrust blocks, shown at the opposite end of the machine, and controlled by the hand rail (which stretches across the machine) for starting and stopping. The friction pulleys can be slid to drive at any part of the horizontal diameter of the friction plate, so that either the speed or direction of rotation (for winding on or stripping) can be varied Across the front of the machine are wooden tension rails or staves The batches of cloth are mounted so that the pins of the batch roller can revolve in bearing supports and the cloth is threaded under the bottom stave, the operator suitably adjusting the tension on the batch For stripping and re-winding, the beam is rotated in the opposite direction, and the cloth is drawn off in laps into the bin beneath, which can be wheeled to either side of the frame. It is then wound on again in the reverse direction, and the operator uses a stick to control the tension and make the selvages lie evenly over each other, taking care to stretch out by hand any narrow piece ends. While this operation is proceeding on one of the beams, the other is rolled to the centre of the frame underneath the fallers It is rotated slowly by means of the end spur wheel (in the same direction as it was rotated during winding on of the cloth) by means of a special arrangement of the end gearing. The beam is simultaneously subjected to a traversing motion backwards and forwards to distribute the blows of the fallers evenly over the surface of the cloth. The direction of the rotation is reversible, and is different for the two beams, because of the opposite directions in which they are respectively wound on. The blow of the faller is almost instantaneous, as it immediately rebounds from the cloth. A second or

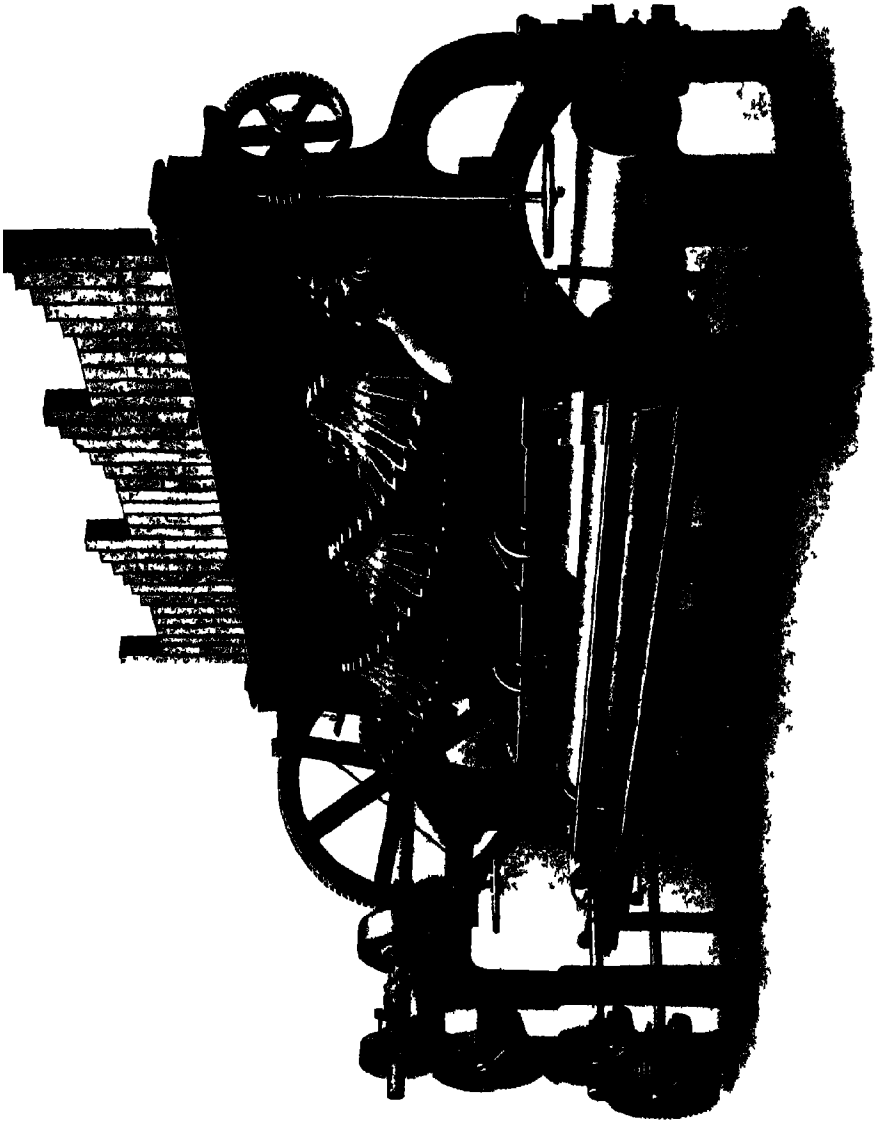


Fig. 229.—Beetling machine.

"recovery" blow is considered to have an important effect and improve the result of beetling. A winding-up rail is used and operated by a hand wheel at the end to raise the fallers from the cloth when they are stopped. Isolated fallers can be pegged up from the bottom guide rail when the space beneath them is bare of cloth, as when the cloth is first wound on, and adjacent widths are spaced apart to allow room for the widening effect of the process.

The pressure due to the blow is essentially of an elastic nature, as distinct from that which occurs in calendering. The effect has been imitated by means of eccentrically operated hammers supported on springs to maintain the elastic character of the tap and to increase the speed of operation.

Where wood fallers are used, as is almost universally the case, the best material is beech It must be thoroughly seasoned to render it capable of maintaining a smooth, hard surface on the striking face and avoid excessive wear at the guides. A stock of fallers should be kept in a well-ventilated shed and periodically restacked to rectify any tendency to warping. The ends are covered with paint to prevent them from cracking, and they are faced up and morticed for the tappets as required. The distance between the bottom of the tappet and the striking face must be kept uniform and be suited to the design of the wiper cam, as mentioned above.

In a now obsolete type of beetling machine the fallers or hammers were operated somewhat after the manner of the well-known steam hammer. The latest or pneumatic type of beetling machine is an improved adaptation of the same principle, and presents several important advantages over the ordinary gravitational system of operation.

Such a machine by the Pneumatic Beetle Co. of Rawtenstall is illustrated in figs 230 and 231 The latter, sectional drawing, clearly indicates the arrangement of a pair of the pneumatic elements, each of which consists of two cylinders and pistons. One of these (F) carries a beechwood block A, serving as striking face in an analogous manner to that of an ordinary faller. The motion of the eccentrically operated piston is transmitted to the striking ram by the compression of the air in the intervening space, and the return stroke by the corresponding suctional effect. The nature of the blow is obviously dependent on the proportioning of the two cylinders, the speed of the eccentric shaft B, and upon the stroke of the ram. These have been proportioned, so that an equivalent effect to that of the ordinary faller is obtained, but at the rate of some three hundred blows per minute instead of the usual seventy or thereabouts. This represents a proportionally greater output.

The reason for the low rate of seventy blows per minute for the ordinary beetle faller was seen to be due to its dependence on gravity for the production of a suitable quality of blow, which must be of an elastic nature.

Fig 230 shows the general arrangement of the machine complete with driving and traverse motion and winding and stripping cones. The former motion is thrown out of gear during the filling and emptying of the beam.

Owing to the duplication of the hammers both beams can be operated simultaneously, whereby a further increase in the output is effected to that due to rate of striking.

A series of air valves shown at the base of the cylinders affords control of the air supply either for arresting the motion of an individual hammer or by means of a non-return valve for replenishing the charge of air which may have become depleted through leakage.

Owing to the arrangement of the hammers on the underside of the beam, improved lighting conditions are obtained for the examination of the finish, but

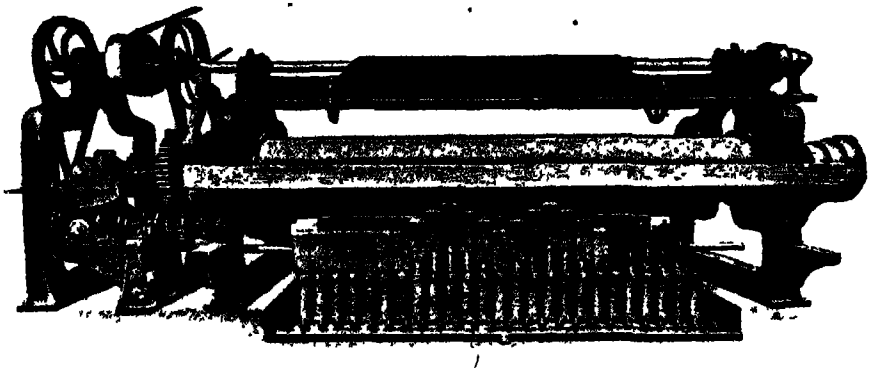


FIG. 230.—Pneumatic beetling machine

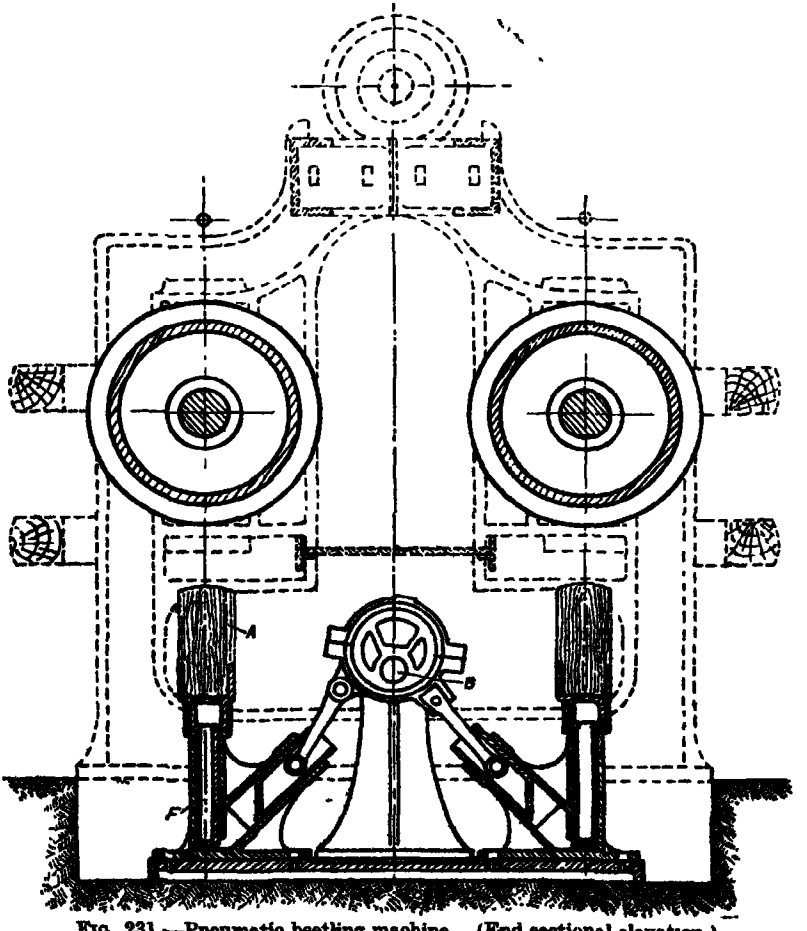


FIG. 231.—Pneumatic beetling machine. (End sectional elevation.)

the effect of the stroke is not quite the same as in the ordinary beetle, owing to the relative slackness of the cloth on the underside of the ram. This may be compensated for by lighter winding or rewinding as the slackness develops.

A great advantage lies in the elimination of the ordinary long fallers owing to their higher initial and maintenance costs, and the inconvenience of handling them for repairs

To appreciate the significance and scope of beetling it is desirable to consider the effects of certain stresses and strains somewhat generally, and this would also throw some light on the processes of calendering which follow.

Stress (or pressure, however applied, produces some corresponding strain (change of form) in the cloth. The initial tendency of pressure upon cloth is to squeeze it in the direction of this stress. The resulting strain is accompanied to some extent by strain in other directions, according to the plasticity and so forth of the material or filling, and these qualities also affect the permanence of the results effected. Hence the significance of "condition" and nature of filling. All these factors are affected by the nature of the stress, *e.g.* its direction, degree, duration, and the medium through which it is applied.

For instance, the effect of passing suitably conditioned and impressionable fabric through a hard nip in a mangle or calender is to apply a uniform pressure across its face and squeeze the threads uniformly The lateral extension of the piece will be negligible, and that of each thread will depend on its elasticity and the space in which it can expand Failing elasticity, it will simply be compressed, but elasticity will be conducive to recovery of original form when the pressure is relieved. The present subject is, however, the nature of the stresses in beetling.

The taps of the fallers are applied uniformly, but not simultaneously, and permit scope for lateral extension of the cloth. The degree of pressure at each tap is definitely proportioned to the weight of the faller (usually about 60 lbs.) and its distance from the cloth when in its top position, and this distance depends on the depth to which the cloth is wound on

The resulting finish (to be regular) must be the same as that which appears at the centre of the roll, so we may confine attention to that fold of the cloth.

The medium through which the pressure of the blow reaches a fibre in that fold is, of course, cloth. The denser (more tightly wound) the medium, the less pressure will be dissipated and fail to reach that fibre By continued analysis of the conditions present, we may deduce the following conclusions .—

That the blows of the fallers, acting through cloth, impress a like formation or "clothy" surface to the mean lap (which represents the average effect after the reversal of the ends for the second process) The shallower the winding, the greater will be the impact and milling effect on the fibre, and it will be the more compressed and harder. The surface will be less clothy or thready, and the effect of brightness which accompanies compression and friction will be more evident.

Conversely, the deeper the winding, the more clothy, thick, and dull will the finish be.

Considerable duration of the process (which on a rough average lasts thirty minutes the first time, and thirty to forty minutes the second) is necessary to produce these effects by means of taps, which are successively applied at a large number of points on the outer surface of the roll. Further, the effects produced on the outer layers are greater than on the inner ones. There must therefore be a time relation between the required treatment for inner and outside laps to

effect uniform results, but this is not governed by any definite rule, and requires actual practice to determine

The goods for beetling are usually separated out in bunches of from two to five pieces, say after conditioning, and then wound on to the beam and beetled for about thirty minutes, the width and effect being noted and compared with the pattern If the result is satisfactory (allowance being made for the effect of the second operation), the stripping and rewinding are then proceeded with and beetling continued till the desired effect is completed in about the same time as was taken for the first operation. Judgment is thus required in determining when the process is half accomplished. A medium length of cloth for wrapping on is three pieces of 100 yards

Owing to the somewhat costly nature of the beetling process many attempts have been made to reproduce its effects by more economical and rapid methods. The most noteworthy of these alternative processes is that of "chasing" on a calender The following may also be mentioned in this connection, viz. swissing, jacking, chesting, and stone mangling. These terms are explained in the section dealing with calenders, but their effects may be here briefly compared with those of beetling.

Swissing on a calender can be made use of either to give a hard, bright finish with threads more or less closed by flattening, or the finish may be comparatively mellow and silky, with less closing and flattening In either case there is no gain in width nor rounding of the threads as in beetling

Chasing affords the most serviceable alternative to beetling, being practically as easy as swissing, but adding the thready effect which the other lacks. There is, however, again no increase in width. In other respects the imitation is sufficiently close to enable the process to be often substituted for beetling Chasing is also used, after a beetling process of sufficient duration to recover width, to augment the other effects of beetling.

Jacking extends the application of the principle adopted in beetling and chasing of applying pressure through a series of folds or thicknesses of cloth, which is first calendered and then rolled up into a batch between two bowls, and sustaining the pressure between them

The stone mangle is an adaptation of a primitive type of mangle, in which two batches of cloth, on iron batch rollers, serve as rollers upon which is mounted a heavy stone-weighted chest or a block of stone. This is caused to travel backwards and forwards, and its weight, coming upon the supporting batches, imitates the later stage of the jacking process. Though slow and cumbersome, this method is still occasionally used.

In a variation of the two above processes the batches are introduced bodily between the nip of two heavy bowls, instead of being wound up while in the nip.

The introduction of the batches in the more modern machines of this type is effected by mounting the rollers or beams on a revolving framework. This carries, say, three such beams at equal distances apart, and so disposed in relation to the nip that while one beam lies between the nip, the preceding one is being furnished with, and the succeeding one stripped of, its batches.

Chesting.—This means the successive wrapping of the cloth in the batch form round the bowls of a calender or heavy mangle instead of round an independent batch roller. In a chesting calender it is necessary to provide arrangements for running in either direction, to wrap or unwrap a batch, or transfer it from one bowl to another. An independent adjustable roller is sometimes employed for this purpose. In all these alternative processes, except swissing, it will be noticed that two or more layers of cloth are subjected to mutual pressure.

The effect of beetling appears to depend upon the absence of oil, fat, or wax. Fort (*J. Soc. Dyers and Col.*, 1921, p. 162) states that this is the case with many kinds of linen and cotton goods, and especially with damasks and sheetings. The finish on these goods is frequently mainly due to the response made to a severe beetling treatment In order to obtain a well-closed appearance and firm, thick handle, beetling must be thoroughly effective. The condition as regards moisture in the cloth, time and temperature of the treatment, and the type of beetles used, and other important factors, all exert a due effect. But, in the course of a prolonged investigation into the causes of unequal beetling properties, Fort found that mere traces of residual oil, wax, or fat could virtually inhibit beetling in either cotton or linen (p 300). He has recorded also (*J.S.C.I*, 1918, 121A) an interesting case of the mechanical powdering of cotton during beetling, referred to on p. 125.

In further experiments, made by Cross (*J.S.C I*, 1920, 58A), normal bleached cotton was damped and beetled continuously in a layer 2 inches thick to the point of destruction In this treatment considerable heat was developed, up to a maximum temperature of 200° C. The following results were obtained on examination of the fibre under the action of sodium-hydroxide solution of 17·5 per cent. concentration :—

	α-cellulose.	β-cellulose	Hygroscopic Moisture
Original cotton . . .	99 7	0 8	
Half tendered . . .	92 3	4 9	3 6
Fully tendered . . .	78 0	16 2	3 3

These results show that the destroyed fibre was not identical with the fine powder described by Fort.

In a later paper (*J. Soc. Dyers and Col*, 1924, p. 142) Fort states that this mechanical powdering of cotton is a distinct phenomenon, and must not be confused with powdering to which chemical changes, such as oxidation or acids, have lent assistance He does not hold the same views as Cross and Bevan The powder obtained by Fort is believed by him to be the product of abrasion of cellulose fibres grinding on each other under limitations imposed by the following necessary conditions .—

1. An unusually close approach to the maximum of close contact between fibres

2. A repeated movement, such as bending, shearing, or twisting of layers of compact fibres.

3 External compression must be maintained constantly to avoid displacement and escape of fibres suffering abrasion on each other

" As regards (1), chalky patches only appear in the later stages of beetling, after the cloth has firmed and gained almost its full measure of compactness. Beetling increases greatly the compactness of the cloth, and it occupies much less cubic space than before beetling. There is no actual increase of specific gravity of the cellulose material of the cloth after beetling, but, according to the degree of dampness and the severity of the beetling, there is an enormous increase in cloth density, and in the actual surface contact of fibres pressing on each other. In the later stages, a state of great solidity exists in the batch of beamed cloth.

" As regards (2), repeated bending of compressed layers of fibres was the

cause of abrasion in the writer's (Fort's) production of powder in beetling, the actual cause of bending being an old wooden beam, with cracks radiating from the core, so wide as to be past wedging, which is the ordinary method of prolonging the life of an old beam

"Condition (3) is really supplementary to (1), but it is just because it is so rarely the case that great compression of fibres in textiles is maintained to create a maximum of close contact between them, while a bending or other frictional movement is taking place repeatedly, that so little has been heard of powdering. One particular beetling machine repeatedly produced powdered patches. The powdering always occurred at the same part of the beam, and the layer of beam covers next the beam, consisting of partly scoured and bleached linen cover cloth, also developed powdering The beam exhibited the defect already described, at one place only, near the end, where the powdering always occurred."

CHAPTER XXXV.

CALENDERING.

THE process of calendering, in a general sense, consists in subjecting the cloth, when suitably prepared and dried, to pressure between rollers or bowls of various descriptions The effects produced depend upon the nature and sequence of the nips, and the quality and preparatory treatment of the cloth The chief effects aimed at in calendering include (as regards appearance) the following —

Glazing and brightening.
Flattening.
Closing
Giving a thready or clothy appearance.
Embossing and allied effects

Effects relating to the feel of the cloth include—

Smoothness.
Threadiness
Hardness and firmness
Elasticity
Mellowness or softness

The relations between these effects and their causes are considered in detail subsequently. We must first, however, refer to some general considerations and apparatus.

The essential features controlling the effects produced at any nip are—

(*a*) Degree of pressure existing between the bowls and, to a certain degree, their temperature.
(*b*) The surface properties of the bowls as regards smoothness and elasticity.
(*c*) The physical properties of the fabric under treatment, and its ingredients

(*a*) represents the sum of the weights of the bowls lying above the nip, together with the pressure due to the compounded weight levers.

The nature of the pressure is slightly elastic in virtue of any such quality in the bowls, and in so far as the weights are at liberty to move vertically.

When " dead set " is applied, by locking the levers and tightening the thrust blocks, the remaining elasticity due to the nature of the bowls is almost neutralised, and in any case it is extremely small. This device is chiefly adopted in small and embossing calenders.

(*b*) The bowls being cylindrical, the contact between the bowls and the cloth at the nip is that between straight lines or very narrow areas extending across the face of the cloth. The width of this area is in inverse proportion to the diameter and elasticity of the bowl.

The smaller the area, the more concentrated is the application of pressure throughout that surface, or the keener is the nip.

Fig. 232 illustrates, in a somewhat exaggerated manner, the distributions of pressure, or relative degrees of contact between the respective faces of a piece of cloth (*a*, *b*) and hard bowls.

Fig. 232 (*a*) illustrates the increase in effective area of contact due to assumed elasticity in the smaller one. The contrast would be still more marked in the case of elasticity in the larger one. As cloth lacks rigidity, the above conditions exaggerate the actual occurrence but help to illustrate a fact– the effect of diameter and elasticity in the keenness of the nip.

The smoothness of the finish depends on that of the surfaces of the bowls, and the compressing and smoothing effects of a hard, smooth, inelastic bowl are necessarily greater than those of a more elastic and softer one. Speaking generally, the impression produced is the outcome of the pressure, the medium and area through which it is applied.

The analysis of the various forms of mechanical impression due to different

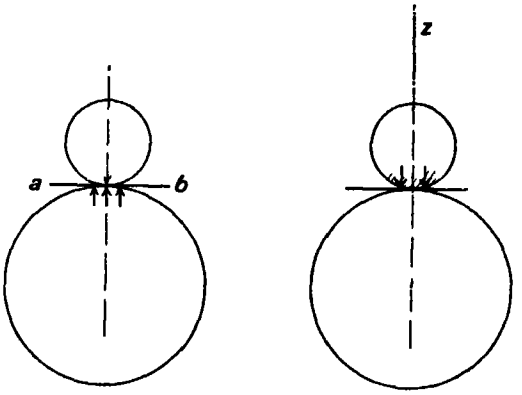


Fig. 232

forms of bowl and the classification of their effects presents little difficulty, but the capacity of the cloth to receive or retain these impressions is a wider subject

Conditions affecting this are—

1. The " condition " or humidity of the cloth
2. The thickness, strength, compressibility, and elasticity of the material.
3. The physical properties of the ingredients incorporated with it
4. The previous history of the cloth, or the extent to which it has been already wrought upon, and its physical properties modified, by preliminary processes.

It is obvious that the degree of humidity of the cloth or its filling must affect the plasticity and cohesion of the constituent particles, and that these affect the reception and retention of the imposed impressions. When the material is dry there is, for example, liability to crushing and fracture These fracturing effects are utilised in " breaking down." But the material may be conditioned to gain elasticity, which causes it to approach its original form when the pressure is released.

There is a further degree of condition which is most favourable for the increased reception and retention of the impression applied at the nip, but excess

of moisture destroys the capacity to retain the effect. To produce a glaze the material must be in that condition which most favours the compression of the material on the face of the cloth, by the smooth metal bowls, into a smooth homogeneous layer.

Respecting the general mechanical arrangement of calenders, it is seen from the accompanying illustrations that this consists of a pair of side frames similar to those of a mangle, and the same appliances for supporting and regulating the weight of the bowls. The cloth is led in through tension rails and over a revolving expander to keep out creases and maintain the width. The peculiarities of special calenders are mentioned later.

The bowls used are distinguished as "soft" and "metal" bowls. The former are built up of a series of cotton or paper washes (paper producing the harder surface), which are threaded over a metallic core and very tightly compressed between strong end-plates under hydraulic pressure. The plates are meanwhile secured in position by means of keys which make a self-tightening conical joint (see fig. 233). The driving bowl is generally a metal one, and third from the bottom, it is of comparatively small diameter, to reduce the torsional strain

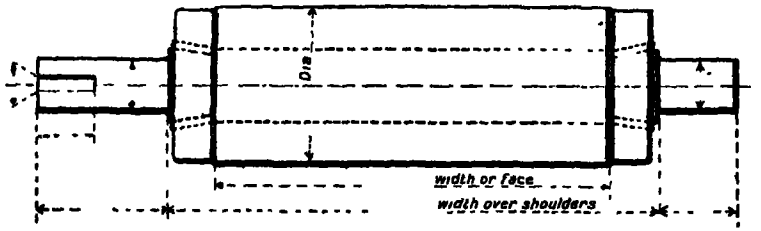


FIG. 233.—"Soft" bowl.

on the driving shaft The rolling motion is imparted to the others by their frictional grip, the pressure between them being adjusted to prevent slip

If, however, a rubbing or frictional effect is required, this is provided by means of gearing, as in the case of a friction mangle. The internal heating of one or more metal bowls is employed in part to maintain the bowls in good and uniform condition and to dissipate any condensed moisture. It is used in special cases, in a manner analogous to domestic ironing or burnishing, assisting to fix or set the physical condition which has been imparted to the cloth in passing through the nips Care must be exercised in its use where the filling contains any chlorides, which are liable to decomposition, with evolution of hydrochloric acid, in the presence of high temperature.

All calenders are arranged with removable gap pieces on one cheek of each frame to facilitate the alteration of the arrangement of the bowls. The metal bowls include brass, fine-grained cast iron, chilled iron and steel. They are supplied with a hollow centre when required for heating. Brass and chilled steel are the most convenient on account of freedom from rusting. Chilled iron is best in a friction bowl on account of its retention of polish. The range of bowls, including cotton, paper, brass, and steel (in order of hardness), affords a wide assortment from which to effect any desired combinations of nips. The bowls are trued up and burnished to a fine glazed surface, and must be kept scrupulously clean, truly bedded, and free from the least risk of marking by the access of any grit, etc., which can effect considerable damage.

The sequence in which the bowls are arranged varies considerably, according

to the finish required, but the considerations already cited indicate some of the principles by which the effects of the separate nips are ascertained. It becomes a simple matter to mount the bowls to give any desired combination of nips. Thus, taking a simple example with five bowls alternately of cotton and metal, one face of the cloth gets four cotton nips, and the other four of metal, as shown in fig. 234. In this case the side *b* is subjected to the maximum treatment possible in a single passage through this calender, and the contrast between the treatment accorded to the two sides is also the extreme one. The governing principles in the choice of nips for specific purposes are more fully illustrated later; but it may be mentioned that predominance of metal nips is conducive to hard, bright, well-closed effects and flattening of the thread. Metal bowls are not mounted contiguously, as the pressure would be too severe for cotton goods So cotton or paper bowls intervene on account of their comparative elasticity.

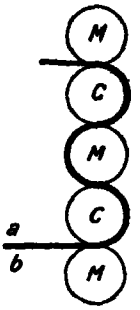


FIG. 234.

Fig. 235 shows a type of calender which is adopted for the most usual classes of work, known as swissing and chasing respectively. Swissing means running the cloth straight through the nips in series, and represents the normal process of calendering when it is desired to smooth and brighten the cloth and more or less close up the threads by flattening and produce either a hard or mellow finish. Chasing has been explained in connection with the water mangle. The result of chasing is the same in both cases, viz. to give a thready appearance, as well as closing the threads and giving a degree of firmness to the cloth as distinct from actual hardness. But the effect is more final in the dry calendering process. The number of bowls in a calender may vary from three to twelve. The most generally useful numbers are three, five, and seven; but if an extra brightness be required, as in the case of cambrics, nainsooks, mulls, etc., a ten-bowl calender is preferred. The following arrangements may be mentioned: To slightly smooth and brighten the face of light (stentered) goods, a small brass bowl between two cotton bowls is used, and the cloth is, of course, run through dry. The effect partially includes that of "breaking down" the finish, by bending the cloth past the tension and scrimp rails and round the small bowl and slightly crushing the starch, supposing it to have been dried up somewhat harsh and rough.

The various arrangements of hard and soft bowls in the intermediate sizes of calenders are too numerous to treat in detail, but the following arrangements may be mentioned as suitable for a large variety of shirting finishes, using the initial letters for the bowls and starting at the top bowl. (C=cotton; P=paper; M=metal.)

1. For soft, dull finishes, C C P C M C M.
2. For hard, bright finishes, C C M C M P M.
3. For hard, bright finish for light goods, such as nainsooks, mulls, cambrics, C C P C C C P M P M.

Fig. 236 shows a seven-bowl calender which is applicable to swissing, chasing, or friction finishes by adjustment of the external gearing.

When it is desired to apply "friction" the bottom (metal) and the third (metal) bowl are mutually geared to revolve at different peripheral speeds, and the upper bowls are raised out of action.

The speed of the upper metal bowl exceeds that of the lower one by an amount varying from 50 to 300 per cent., according to the degree of polish required.

The cloth travels at the speed of the two lower bowls, and the upper metal

bowl, which is heated, is termed the friction bowl, as it is the one which effects the frictional burnishing and smoothing of the upper surface of the cloth. There are

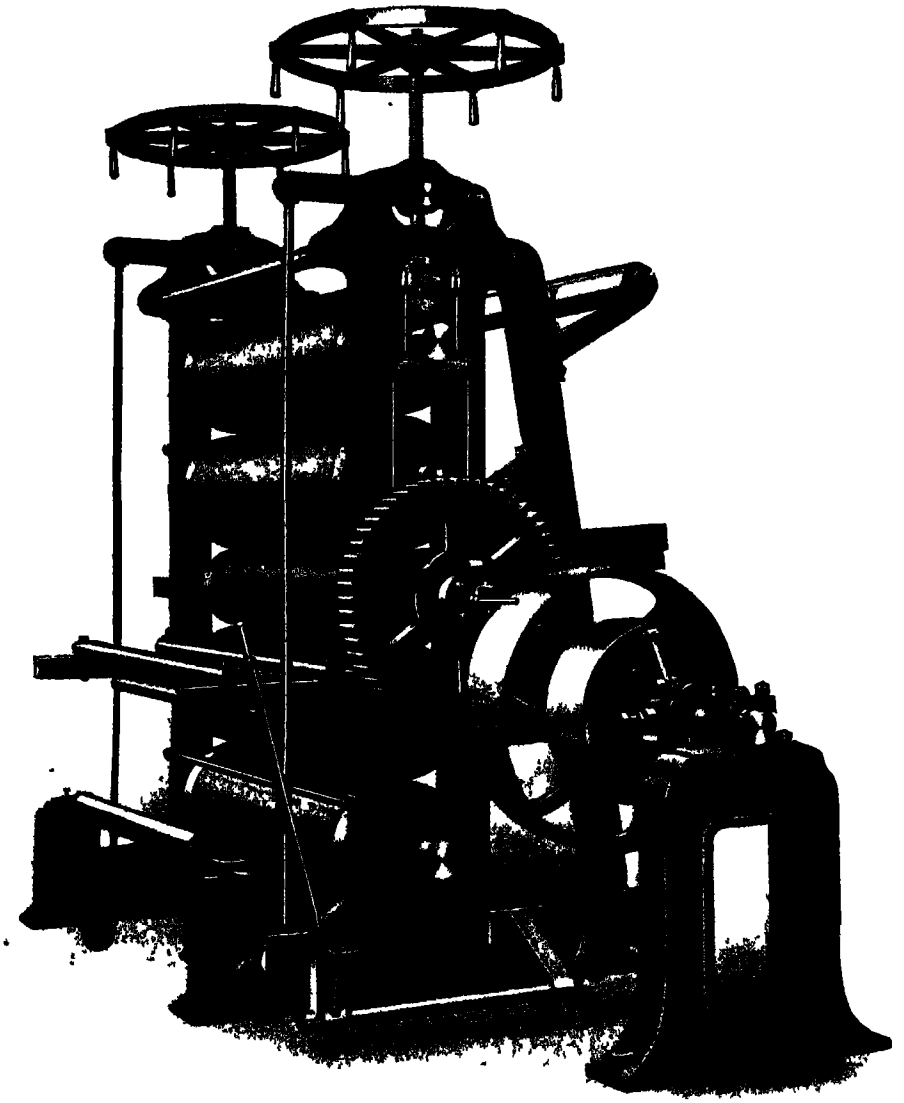


Fig 235.—Five-bowl chasing and swissing calender.

several methods of arranging the bowls in friction calenders. Thus the friction bowl may be placed between cotton or paper bowls geared for friction at the first nip for light frictioning, or the two outer bowls may be geared for equal, and the intermediate (metal) friction bowl geared for higher, peripheral speeds, so

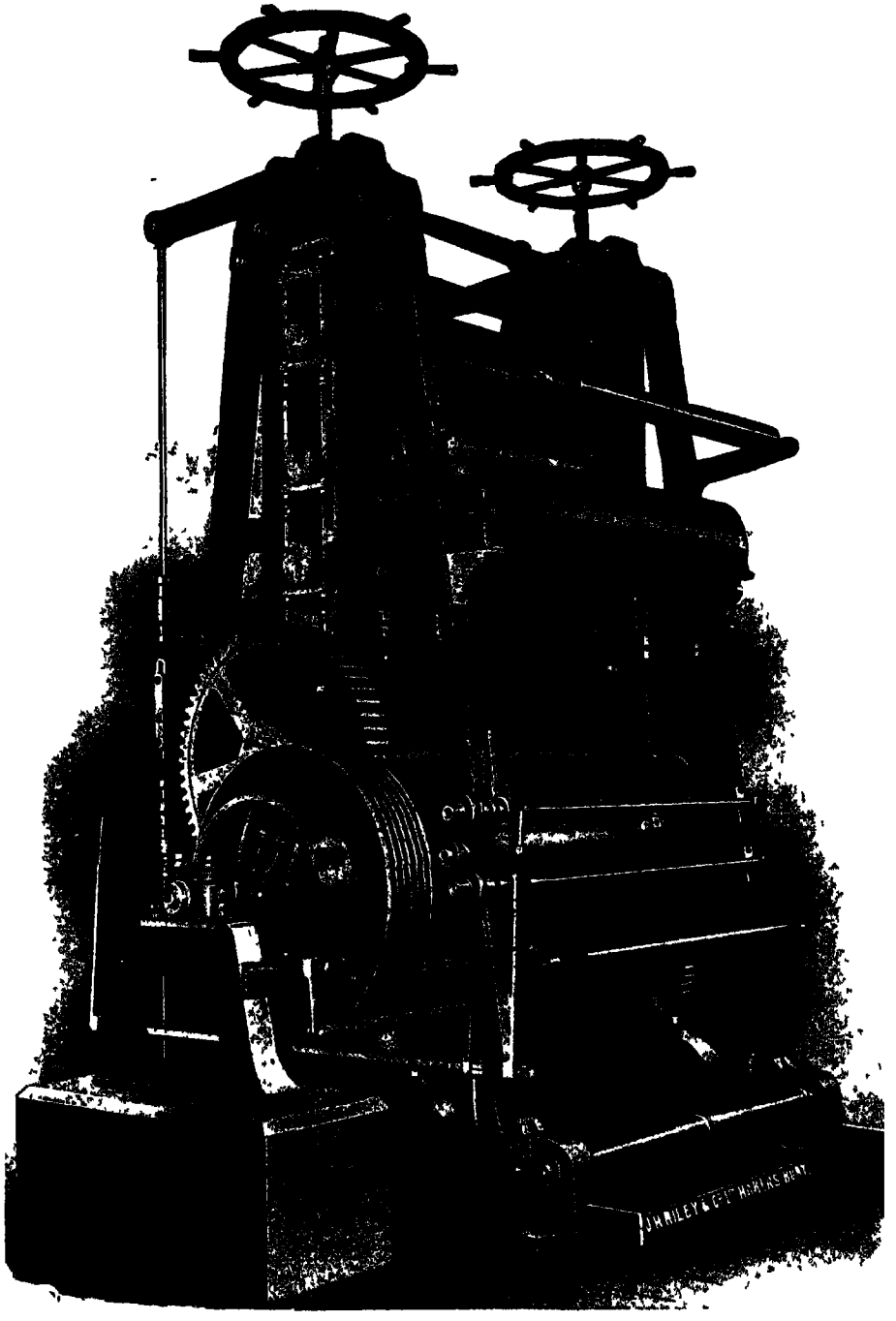


FIG. 236.—Seven-bowl calender.

that both nips present friction. It is desirable to pass the cloth round an external guide roller between its first and second nip in order to vary the point of contact between intermediate bowl and cloth in the first and second nips. In a heavy friction calender suitable for closing or glazing, tracing, binding cloth, etc., where extra closeness of texture and filling is required, the bottom bowl is of close-grained cast iron and geared with the (top) friction bowl, which is gas-heated. The latter is made of the same material or of chilled iron, and highly polished. The middle bowl is of hard-pressed paper. An adjustable roller above the friction bowl is of cast iron, fixed and adjusted in close contact with the friction bowl, to regulate the distribution of a film of lubricating grease which is sometimes applied to the face of the bowl.

Steam-heating is suitable for most friction calendering For very heavy work, such as the above mentioned, gas-heating is, however, generally employed.

The closing effect of friction is more thorough than any other form of calendering. The corresponding condition conducive to glazing is that the surface properties of the cloth be such that the constituent particles may sustain compression, resulting in very uniform and compact association.

An embossing calender embodies the very reverse condition to that of frictioning, as it is most important to keep the engagement of the bowls and embossing roller in uniform relation to the cloth. Machine-cut gear wheels are consequently employed in some of the calenders to ensure equal peripheral speeds of cloth and roller. The running on and off tackle is likewise controlled with the same object, and the degree of pressure between engraving roller and cloth definitely adjusted by screws with fixed nuts instead of weighted levers. The centre roller is heated and variously made as a permanent steel shell or capable of accommodating interchangeable copper engraving shells. The Schreiner calender is an embossing calender of a special type to give a peculiar lustrous effect. This arises out of impression under heavy pressure of a series of ridges into the cloth, whose corresponding formation is engraved in the upper bowl in a diagonal direction.

The jacking calender, previously referred to in connection with imitation beetling, consists of a four-bowl calender (fig 237), similar to the finishing frame already described The cloth passes through the nips of the three lower bowls (cotton, paper, cotton), and is then tightly wound on a batch roller between the rolling surfaces of the upper cotton and the top (paper) bowl, as well as being in contact with the cloth in the batch. Meanwhile the cloth in the batch continues under the same pressure, becoming closed and brightly glazed.

A convenient method of applying the pressure in the machine is by a downward pressing hydraulic ram applied to the necks of the top bowl. As the diameter of the batch increases, the hydraulic pressure remains uniform, but the accommodation for the increasing diameter is effected by the expulsion of water from the cylinders of the rams through a suitably adjusted pressure valve.

A novel form of calendering machine, shown in fig. 238, illustrates a means of imparting a good lustre without applying any considerable pressure to the cloth. This machine, by Sir James Farmer & Sons, Ltd., is especially suitable for the treatment of striped and ribbed cotton and mixed goods, which require simultaneously a good face lustre, a soft feel, fulness of thread, and that the pattern shall be well raised.

The lustre is produced by passing the cloth (which is suitably conditioned) successively under two highly glazed hot iron calendering bowls, arranged horizontally, and resting with only their own weight upon the cloth. The underside of the cloth rests on soft felt-covered rolls, thus minimising the severity

of the nip. An intermediate guide roller is available for increasing the range of contact between cloth and hot bowls.

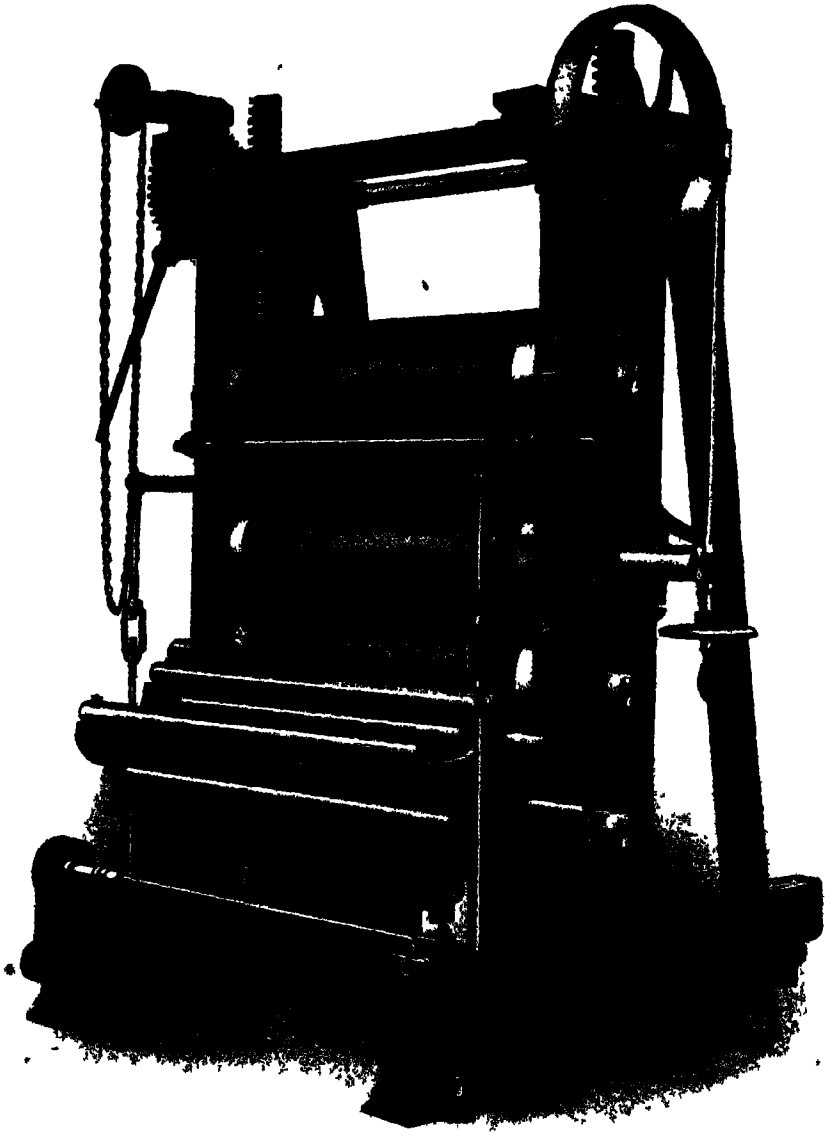


Fig. 237.—Four-bowl jacking calender.

The cloth enters the machine over an expander, then over a hot felt-covered cylinder, or it may first be conditioned by means of a steam jet It then enters the calendering rolls, as described, sustaining a light frictional drag between the

first and second nips. It is finally drawn tightly over a fixed, smooth, steam-heated cylinder on the tallying roller, the object of which is to raise the twill or ribs, which have been partially flattened in the preceding operation.

Huebner and Malwin (*J. Soc Dyers and Col.*, 1924, p. 5) have investigated also the changes which occur in cotton fabrics during calendering and beetling. Two fabrics were used The first ("C") was a high class fabric made from long-stapled Sea Island cotton; the second ("H") was made from American cotton The calendering was carried out on a four-bowl calender as follows:—

A paper bowl on top, a steam-heated bowl next, then a paper bowl, and finally a steel bowl. The second bowl was heated with steam of about 15 lbs. pressure per square inch. The fabrics were passed between the second and third and

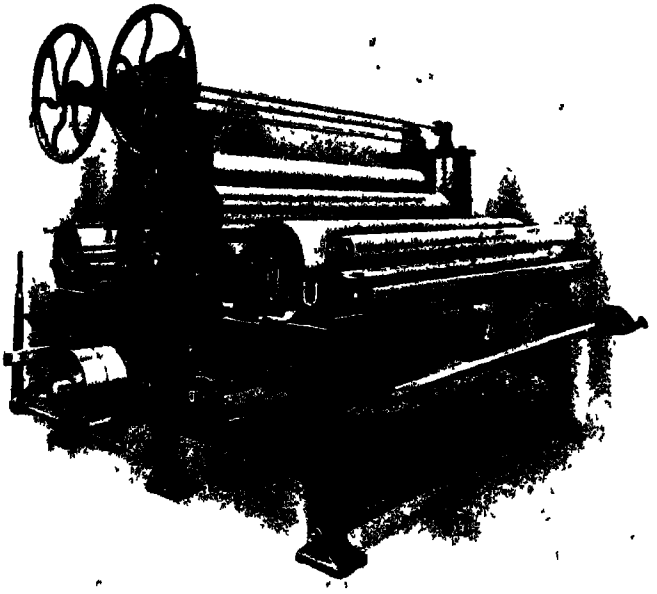


FIG 238.—Natural lustre finishing machine.

between the third and fourth bowls Each passage represented, therefore, two nips.

The results were estimated as tensile strain and ripping strain, that of the original fabric being taken as 100. It appeared that six passages through the calender (twelve nips) caused a considerable increase in the ripping strain in both warp and weft During prolonged calendering, the ripping strain of the fabric increases, but the increase is greater in the weft than in the warp. After forty nips, repeated calendering results in a distinct reduction in the tensile strain of the fabric, which is uniform in both warp and weft The increase in ripping strain of the lighter fabric ("H") was less pronounced than in the more closely woven "C" fabric.

Starching the fabric "C," without calendering, decreased the ripping strain from 100 to 88 in the warp and to 81·4 in the weft, whilst it increased the tensile strain from 100 to 116·5 and 123·5 respectively. No appreciable reduction in the tensile strain of the warp is caused by forty nips, but is distinct after two

hundred. The weft, however, shows a distinct reduction after twelve nips. The effect of starch upon the tensile strain of the "H" fabric is different in that it shows a distinct increase, after calendering, in the warp, whilst in the weft it remains practically constant. Cold calendering does not affect the tensile strain of the fabric as distinct from hot calendering, in which two hundred nips produced a reduction of 16 per cent. in the warp and 15 per cent. in the weft. The effect of beetling was examined in a similar manner The results are given in the following table .—

Hours Beetled	Fabric "C."				Fabric "H."			
	Ripping Strain		Tensile Strain		Ripping Strain.		Tensile Strain.	
	Warp	Weft	Warp	Weft.	Warp	Weft.	Warp	Weft.
0	100 0	100 0	100 0	100 0	100·0	100 0	100 0	100·0
1	127 7	124·0	100 3	102 7	114 0	116 4	96 8	92 9
5	143 6	134 5	98·6	98 8	160 2	151 2	104 0	99 0
10	148 6	161 8	100 6	95 3	163 0	171 7	108 7	100 0
20	163 5	177 9	98 0	99 2	159 1	166 4	100 1	111 0
30	168 2	172 6	98 6	94 0	151 7	162 7	101 9	102 8
40	171 4	183 2	98 8	93 1	143 4	159 5	102 9	91 8
50	169 3	166 8	94 9	93 1	148 6	153 3		

Microphotographs taken before and after treatment showed that calendering increases the diameter of the fibres. The twist in some is flattened like that of dead cotton, whilst in others it is rounded, giving the fibre an appearance like that of mercerised cotton. The diameter of the beetled fibres is considerably increased, and some resemble those of cotton mercerised under tension. Occasionally they exhibit fairly regular impressions, due, probably, to the pressure exerted by other fibres during beetling.

Yarn Finishing.—A large proportion of yarn that is bleached is subjected to no further finishing treatment than conditioning to weight by exposure to the atmospheric moisture or assisted by spraying. It is then straightened out by hand in a similar manner as described prior to drying, and is forthwith "made-up" and pressed into 10- or 12-lb bundles.

Other methods employed in the finishing of yarn in the hank are stretching and calendering (figs. 239, 240), yarns are also sized in the hank and polished after drying by a mechanical process of brushing. The peculiarity of the above finishing machines lies in their necessary adaptation for the manipulation of yarn in the hank

In the calender, which consists of two cotton and a cast-iron top (driving) bowl, the hank is introduced by removing the middle bowl and threading one end of the hank around it. The threads are spread out evenly over the surface, and the same applies to the other end of the hank, which is, however, threaded over a free guide roller. The hank thus rotates around the two as an endless band, and sustains one nip between the two cotton bowls and a second between the middle cotton and upper iron bowl.

Stretching and straightening is effected in a machine consisting of a driving wince or roller, and a stationary hot burnishing plate, over and around which the

hank is made to revolve by the wince. The wince meanwhile undergoes upward and downward movements, thereby gradually stretching the yarn between itself and the hot plate The yarn is thus simultaneously stretched, straightened, and somewhat polished, and it is meanwhile brought to condition.

The polishing of sized yarn is effected by causing it to rotate round wince reels, against which a series of stiff brushes, mounted on a drum, revolve in the opposite direction

The general effects produced by the foregoing mechanical processes may be briefly summarised, and the terms defined.

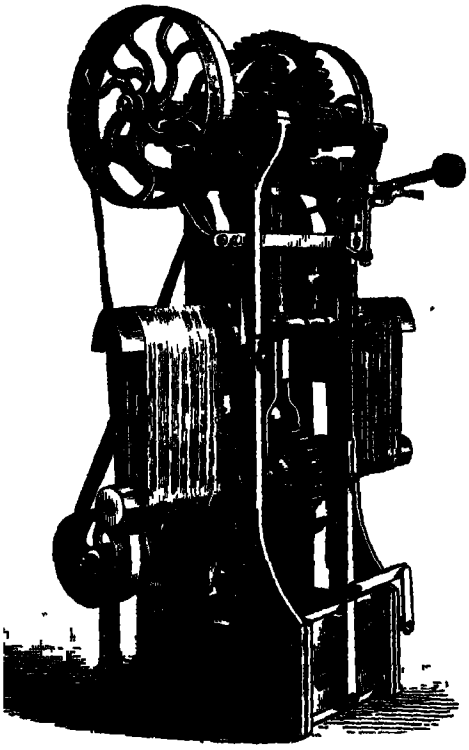


FIG. 239.—Improved hank stretching machine.

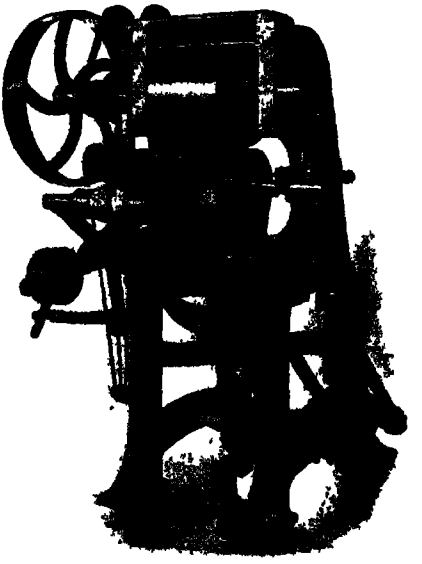


FIG. 240.—Improved yarn preparing machin

The terms lustre, glaze, brightness, although frequently used to denote the same qualities, are also used with the following specialised meanings in conjunction with cloth finishing.

Lustre.—This term denotes a surface quality with respect to reflection of light, which yields a characteristic sheen, or an effect similar to that due to a lustrous fabric, such as satin. The Schreiner finish is an example.

Glaze.—This term is generally confined to that degree of polish produced by friction calendering. The factors affecting the production of glaze are: the smoothness and temperature of the friction bowls; the degree of friction applied; and the properties of the materials used.

Brightness.—Although including, and employed to qualify, the above terms

(*e.g.* "bright" or "dull" glaze), it is generally used to distinguish the various glossy effects produced in beetling and in simple calendering.

The term is also used to a less extent in another sense, viz. to denote superior cleanliness and whiteness in pure or stiffened finishes.

Smoothness is complementary to glaze and brightness, and is determined by the same causes.

Flatness.—This term relates to the degree of compression retained by the threads after a process of beetling or calendering. Although a legitimate and desired result in some respects, such as in the direction of producing smoothness, etc., it is also encountered to an undesirable extent in the process of closing when that process is carried to an extreme, as flattening is accompanied by corresponding thinness, and this, again, by "ragginess," in the absence of a stiffening medium or assistant, in the cloth; but in the latter case the reverse defect, known as "papery" feel, is liable to occur.

Closing.—This means the reduction or filling up of the gaps (or "grinning" effect) between consecutive threads, such gaps being due to the lowness of the count of the cloth, or to its previous treatment. When closing is chiefly developed by vertical compression, the action is accompanied by a greater degree of flattening than is the case with chasing or beetling, and the defect previously referred to is liable to ensue. The necessity for closing without loss of thickness is one of the main reasons for the introduction of filling materials, as closing is then partially effected by mere filling, and in some cases entirely so.

Thready and Clothy Effects.—Both these effects are induced with the object of maintaining or simulating the properties which are associated with pure cloth.

Threadiness refers to the production of undulations in the surface of the cloth to bring out, or imitate, the disposition or lay of the interwoven threads which constitute the fabric, and as they would naturally appear at the surface of the cloth. The effect is developed in the operation of "raising" (not to be confused with nap raising), beetling, and chasing. The term applies whether the effect be produced on a pure or starched face

Clothiness.—A finish may be clothy either with respect to its appearance or feel. Thus, threadiness conduces to a clothy appearance and to a superficial clothy feel. But that does not constitute the complete feel of the material. In the remaining sense, a clothy feel should give the impression of suppleness and body, and be equally removed from papery and from limp (raggy) feel.

Predisposing to clothiness of finish are, good quality of cloth to start with, "shrinking," moderate assistance, beetling, mellowing, etc.

Roughness is not a result of calendering, excepting in the form of *threadiness*, which has been considered in connection with chasing. It may be mentioned here that roughness, when required, is obtained by drying up a heavy filling. There are several rough effects, as, for instance, the cockle finish, thimble-top effect, etc.

Hardness is a natural consequence of compression or drying up in the absence of a lubricating principle in the cloth, especially if the cloth be clogged with filling and itself compressed into a hard mass Hardness particularly follows calendering with keen metal nips and weight, as also tight beetling with shallow winding.

Firmness is a degree of hardness applying more especially to cloth having a thick, substantial, leathery feel, and indicates real or apparent strength and substance; the effect is favoured by filling or assisting.

Mellowness and softness are the reverse properties of hardness and firmness.

The only connection between these properties and calendering lies in the process of breaking down described in connection therewith.

Mellowness may be the natural outcome of a finish in which stiffening processes have not been applied, or the result of breaking it down in stretcher, finishing frame, etc., or by wetting out with a softening agent

Elasticity denotes the tendency on the part of the finished cloth, assuming it to have been distorted by bending, of reverting to its normal shape The same property with respect to tensional strain is less marked, as woven cotton cloth, although sufficiently supple, is not in any case particularly elastic, nor can it be rendered so (in the tensional sense) by the addition of materials to it.

Elasticity, as defined above, is induced by the association with the fabric of a suitable dressing mixture. A starch paste of thin to medium consistency may be used, together with a modifying ingredient, such as dextrin, to control its capacity for setting hard or otherwise. The constitution, consistency, and application of the dressing mixture are governed to suit the degree of stiffness required in the finish, and gelatinous or glutinous agents may be added to or substituted for the starch, in accordance with their respective capacities and the circumstances of the case.

CHAPTER XXXVI.

COMBINED FINISHING PROCESSES.

In the foregoing pages finishing has been dealt with from the standpoint of the effects produced by particular machines or processes, and it has been shown how these individual processes may be controlled to develop various effects. But in the majority of practical instances the ultimate properties of the finish are the outcome of several of these processes, and their final effect depends very much upon the method and order in which they have been respectively employed.

This fact is illustrated in connection with the table given on p. 676, as also in the practical examples of processes applied to goods of various kinds.

Since the effects of any combination are complex, and depend on several factors, all of which are variable, it is not easy to give formulæ of runnings which are capable of general application. The factor which most prominently qualifies the effects brought about by a definite combination is the character of the cloth which is being treated, and when somewhat dissimilar fabrics are being dealt with for a similar finish, it follows that the one of inferior quality will require some differential treatment Thus, in the common case of a pure, home-trade finish, in which the object is to give the impression of a finely woven fabric resembling linen, and in which the beetling process is a prominent element in the treatment employed, the closed appearance in the superior cloth will be the more readily effected without corresponding drawbacks, while the inferior, if closed to the same extent, will develop an undesirable flat, thin, and hard effect The difference will be the more marked according to the variation in the qualities of the two samples. These differences must be counteracted by recourse to some treatment tending to make the inferior cloth more similar to the better one, whose threads are more closely woven and possibly consist of superior yarn. One way of doing this is to allow the natural shrinkage of the lower cloth to take full effect, if the specified finished width will allow, and to apply a small quantity of thin starch, so that, after conditioning, the threads will become more swollen In virtue of the shrinkage that has been permitted, they will be already closer together, and the subsequent effect of beetling will thus be modified in the desired direction.

Thus, the weight and count of the grey cloth largely control the character of the finish that will be produced by a given combination of processes, and, as in the case cited, will also determine the effect produced in one or each of the processes

The classification of finishes may be based either upon the routine adopted in their production, or upon the quality of the finish. As definite finishes frequently refer to definite qualities of cloth, the two methods often bear some relation to each other.

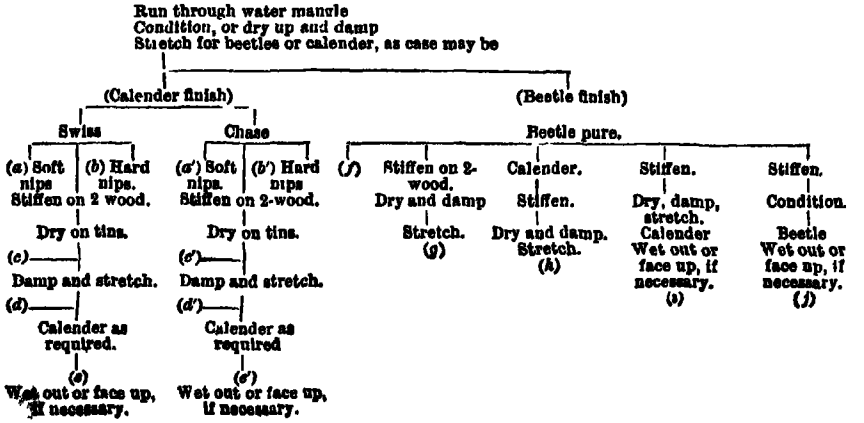
The determination of the qualities of the finish is ultimately a matter of

comparison, as to appearance and feel, with a pattern which must be taken as the standard. With these qualities must also be considered conditions relating to count, weight, and width before the finish is fully defined. In the so-called Standard Finishes, which are designated by various names, letters, trade marks, etc., the quality of the finish by long familiarity has acquired a fairly definite significance, and become associated with a recognised combination of processes as regards its production Other finishes, which are new to a finisher, become by that fact "Standard Finishes," and he must reconstruct a suitable scheme for reproducing the same by means of such evidence as the pattern and the other specified conditions afford. The most convenient and rational way of describing such finishes is in terms which combine the appearance and feel, and the class of material represented by the pattern, and then, by deduction, the general type of process which the pattern suggests or definitely indicates to experienced observation.

These items having been recorded, together with the details mentioned above, an experimental scheme of runnings is applied to the bleached cloth, and its effects noted from stage to stage. The necessary corrections are introduced, or allowed for, in a second trial piece, and the finish is thus standardised This operation of sampling calls for the greatest care and accuracy in observing and recording the conditions which successively arise, as not only are definite adjustments of the proportions of the finishing mixture required, but the conflicting effects of shrinkage or extension must be allowed for, as a definite width is one of the conditions which must be satisfied within narrow limits

Many of these interdependent effects have been discussed, and it is endeavoured to further illustrate them in the following table and examples; but the object here, as elsewhere in this treatise, is rather to indicate general principles than to formulate working instructions.

The table given represents, in condensed form, the relations which individual processes bear to each other, and how they may be combined to assist in the production of various effects. It must, however, be borne in mind that any attempts at generalisation of this kind are necessarily subject to such limitations as have been pointed out from time to time, also that comparisons effected on such lines are only valid when based on their application to similar goods. In all cases of finishing, success depends as much on intelligent adjustments to meet constantly varying conditions, as upon the use of formulæ for makings or runnings



(*a*) Finish is pure, mellow, silky, slightly closed

(*a'*) Finish is pure, mellow, duller, thready, better closed.

(*b*) As (*a*), but firmer, brighter, threads flatter and better closed

(*b'*) As (*a*), but firmer and better closed.

(*c*) (*c'*) Relatively thick and hard; face dull and rough as compared with preceding finishes, and according to degree of stiffening.

(*d*) (*d'*) Differ from (*c*) (*c'*) in increased width and mellowness, according to use of stretcher.

(*e*) (*e'*) Finish depends on method of calendering, and can be modified for hardness or mellowness, flatness or threadiness, and brightness, as in the case of (*a*) (*a'*) (*b*) (*b'*)

Assuming equivalent treatments in this process, (*e'*) will be better closed and somewhat more clothy than (*e*).

According to degree of stiffening the appearance and feel of these finishes may vary from apparent purity to heavily starched (rough or smooth) finishes The latter extreme is made more evident if F or BF mangles be used in place of two-wood

In shrunk finishes, stretching is suppressed or omitted, resulting in better closed and more substantial appearance The object of wetting out or facing up has been described.

(*f*) Finish is pure, well closed, width increased, and effect mellow, clothy and dull, or harder and brighter, according to depth and lightness of winding on and condition.

(*g*) This terminates the process for the "R finish." Effect thicker and duller than (*f*), in accordance with degree of stiffening and stretching, which also control degree of firmness.

(*h*) The initial beetling effect is extended or modified by calendering. Thus chasing, after beetling, accentuates closing and clothy effect and is cheaper than twice beetling. Swissing, after beetling, superimposes flattening effect, the more so as nips are hard and keen See subsequent notes as to effect of calendering after stiffening. The finish of (*h*) will be more or less dulled by stiffening and stretching, as in (*g*).

(*i*) The tendency (while increasing substance and filling up pores by stiffening) is to obscure the starchy appearance by inverting the sequence of calendering and stiffening, but the preparatory effect of calendering on stiffening is absent (and requires adding in some cases) The general effect in (*i*) is that the final calendering effect predominates. The preliminary beetling has served mainly to effect closing and give width.

(*j*) This is one method for the "S finish," and is essentially a stiffened beetle finish. It derives the full benefit of beetling for closing, and brightening and yielding the best approximation to the character of pure cloth of better quality than it actually is The facing up is to obliterate water-marks and smarten and smooth the surface, and relates to treatment in the finishing frame.

Note.—Allowance must be made for the varying effects of more or less condition in the cloth and modifying effects of finishing ingredients.

Finishes may be broadly classified as being either pure, assisted, or stiffened.

Pure Finishes.—*In this category are included goods, corresponding to the* madder bleach previously referred to, which undergo the subsequent processes of calico printing and dyeing. Prior to their delivery to the print-works, the only finishing operations called for are their opening out and washing in the

scutcher mangle, during which attention is paid to the rectification of width and distortions of the threads. They are then dried up and delivered.

Many varieties of goods which are finished pure for the white trade call for additional treatment to that described above. Thus, in the case of domestic calicoes for the home trade, the special requirements are for such treatment as shall improve the general appearance of the cloth, as regards smoothness, brightness, and in the imitation of such qualities as may serve to render the calico similar to finely woven linen. For this purpose the process of beetling is especially suitable, but is largely replaced by the more rapid and less costly process of calendering, or they may be used in conjunction When the necessity is mainly that of smoothing and smartening up the face of the cloth, and imparting a certain degree of lustre, calendering is employed. The pure finishes are closely connected with the assisted finishes, mentioned below, and, as previously stated, it is frequently necessary to resort to a light application of starch to bring out the full effect of the beetling and especially of the calendering operations, or to assist in the retention of these effects. There is, in fact, no clear line of demarcation between a pure and an assisted finish, but it is, apart from any question of chemical purity, an advantage that a cloth should depend as little as possible on the temporary effect of a soluble assisting agent It is for this reason that the very effectual and permanent results of beetling are to be preferred in the preparation of so many pure finishes.

Assisted Finishes.—As explained in the above section, this term relates to the addition to the cloth of some binding or stiffening agent, to give additional effect to the mechanical finishing process employed, or to increase the feeling of substantiality of the cloth The important thing is that the addition must not be too evident

Stiffened Finishes.—This term is applied to finishes in which the addition of stiffening, binding, filling, and weighting agents is more considerably employed, and in a less disguised manner than in the preceding instances. The thing that is disguised is more often the cloth than the filling materials, but a semblance of woven texture is not infrequently imparted to the latter by the production of impressions therein, which are derived from contact with cloth, as in the chasing process As many of these heavily filled goods are not intended for wearing purposes, the problem of making them look like cloth does not arise, and if glaze be required, the process of heavy friction calendering is indicated. The methods of applying the stiffening and filling materials was discussed in connection with stiffening mangles.

For the production of the rougher finishes, the method is to follow the stiffening process by drying up the cloth on the tins, and if the finish is then too rough, it may be modified by breaking down on the stretching machine, or otherwise as described.

In dealing with more moderately stiffened goods, the disguise of the adulterant may be effected by the rather obvious expedient of applying the bulk of it to the back of the cloth, by use of the back-filling or back-starching mangle, whereby the other face of the cloth may be finished to present any desired degree of purity.

Stiffening is not of necessity a device to create a fictitious impression as to the quality of the cloth, as it offers the only means of rendering certain materials either marketable or of use. This will be seen in the case of those goods which are specially associated with stenter and similar finishes, as, for instance, curtains and the like, having an open, figured pattern, the useful effect of which can only be presented, and a pleasing tint imparted, by providing the threads with

mechanical support, and a medium for the reception of the colouring matter. The necessity for mechanical stiffness or elasticity is in many other fabrics in common use sufficiently obvious.

Some of the main characteristics of respective types of finish having now been referred to, the matter of combinations of processes to produce definite types of finish may be exemplified.

Light Goods.—These include a proportion of pure finishes and many for which the stentering process is most suitable. In these goods regularity of width and pattern, softness, or elasticity of finish are of importance, as in the case of checks, lawns, curtains, lappets, etc

The type of procedure adopted is as follows —

1 Wash in scutching mangle.

2 Dry on tins.

3 Stiffen in two-wood or brass and wood mangle, preceded, if required, by three nips in the calender to take off the rawness of the threads and limit the absorption of starch

4. Stenter

5. Calender, if necessary, either to break down, or brighten, as may be required

Example 1.—Brocade for bright, mellow (stenter) finish.

Runnings.—Mangle, dry, three-nips calender, stiffen, stenter (swiss), calender

Making.—Wheat starch, 9 parts, and water, 7 parts, boiled for twenty minutes

Example 2 —Victoria lawns, bright, elastic (stenter) finish

Runnings.—As before

Making.— Dextrin (3), wheat starch (2½), and water (10), boiled for fifteen minutes

Light goods such as mulls, tanjibs, madapolams, nainsooks, cambrics, etc., can be finished more expeditiously by the following methods; stentering being less necessary for maintenance of width or pattern, tin-drying is substituted.

Example 1.—White cambric, soft, bright (calender) finish

Runnings.—Mangle, stiffen wet at two-wood mangle, condition, stretch, calender (ten-bowl)

Example 2.—Madapolam, soft (mangle) finish

Runnings.—Mangle, dry up, assist on two-bowl mangle with a little wheat starch and blue to shade, dry up, damp, and stretch

Example 3 —Nainsook (Indian), bright, mellow (calender) finish.

Runnings.—Five-bowl mangle, dry, damp, stretch, stiffen, dry, damp, stretch, and calender (ten-bowl)

Making.—Wheat starch (1) and water (20).

Example 4.—Pure finished nainsooks and mulls

Runnings.—Mangle, and, if previously well washed, introduce blue to shade in the water-box (otherwise blue in another mangle), dry, condition, stretch, calender (ten-bowl) If the width is recovered at the first mangle, stretching before calendering may be omitted.

Shirtings.—The numerous finishes applied to shirtings, ranging from pure domestics to heavily filled Egyptian and China shirtings, cover a large section of the finisher's range of operations. The requirements relating to domestic shirtings for the home market consist chiefly in the accentuation of qualities, associated with fine, close weaving, substantial but supple feel, and such smoothness and brightness as is consistent with mellowness.

The main problem with such finishes lies, therefore, in the effectual closing up of the threads without inducing excessive flatness and hardness, which are liable to accompany this process, especially when calendering is employed.

Many "pure" finishes are assisted with a little stiffening to add substance and assist in closing, or are faced up with a little starch.

The following sequence of operations is largely adopted: Chase on water mangle, condition, beetle pure, chase on calender, damp, and condition for room (*i.e.* for making up).

Here the beetling process is brought in to effect the bulk of the closing, but this effect is accentuated during chasing. The final damping takes out the water-marks, and conditioning leaves the goods conveniently mellow.

If, however, a definite width is specified in excess of that obtainable above by beetling, the stretching process is called into requisition, and the resulting finish will be inferior in respect of closing and thickness of feel, more especially with inferior qualities of cloth.

Examples of Shirting Finishes.

Example 1.—Medium finish. Known as "R finish."

Runnings.—Water mangle, dry, damp, stretch, beetle pure, stiffen on two-wood mangle, dry, damp, and finish off stretcher.

Making.—Farina (12 parts), china clay (24 parts), solution of Epsom salt (32° Tw) (24 parts), water (85 parts), heat to 140° F

The cloth is assumed to be of good quality (of 19×20 count), and the process is devised to close the threads, increase the width and weight, and produce a dull, mellow finish The stiffening after beetling dulls the brightness and increases the apparent substance of the cloth. The stiffness is broken down as required at the stretcher The inclusion of the conditioning agent (Epsom salt) assists, with the clay, in adding weight, but it also aids in mellowing the finish by retaining moisture.

A variation of this finish, to increase the brightness, consists in calendering the cloth after stiffening and conditioning. After this it is finished off the stretcher as above.

Example 2.—"W finish."

This differs from the "R finish" in introducing chasing after beetling pure, to increase the closing effect The following is an example —

Runnings.—Water mangle, condition and stretch, beetle pure, calender pure (chasing), slightly stiffen on two-wood mangle, condition, to room.

Making.—Maize starch (10 parts), Epsom salt solution (72 parts), glue (2 parts), water (144 parts), heat to 160° F

This process is conducive to a well-closed, dull, clothy, and mellow finish. The humidity retained by the deliquescent balances any tendency to excessive stiffness.

Example 3.—Method of producing a bright beetled finish applicable to (*a*) a low quality cloth, or (*b*) a better and higher count cloth.

(*a*) **Runnings.**—Water mangle, condition, beetle pure (30′ and 30′), stiffen (dry) in two-wood mangle, condition, finish off beetles (30′ and 40′).

Making.—Farina (20 parts), china clay (48 parts), Epsom salt solution (32° Tw.) (48 parts), blue to shade, water (160 parts); heat to 160° F.

(*b*) **Runnings.**—Water mangle, stiffen (wet) on two-bowl mangle, condition, beetle (30′ and 30′).

Making.—Farina (30 parts), china clay (24 parts), blue to shade, water (155 parts); heat to 160° F.

Note.—The difference in weighting materials used, the method of application, and the amount of beetling required are determined solely by the difference in quality of the cloth.

Example 4.—Rough, heavy shirting finish.

Runnings.—Water mangle, dry up, stiffen on two-wood mangle, dry, damp, finish off stretcher

Making.—Starch (30 parts), farina (12 parts), china clay (144 parts), mineral (24 parts), oil (4 parts), water (200 parts), heat to 160° F.

Note the omission of closing; but drying up before stiffening induces the maximum filling; the absence of subsequent beetling or calendering leaves a rough surface. The hardness may be more or less broken down on the stretcher.

Example 5.—Heavy China shirting.

Runnings.—Water mangle, dry, damp, stretch, beetle, stiffen in B F M, dry, damp, stretch, chase in seven-bowl calender, starch in two-wood mangle (using farina (1 part) and water (120 parts)), with face side to starch, dry, cool, damp, and finish off stretcher

Making.—Starch (30 parts), farina (12 parts), china clay (144 parts), mineral white (36 parts), French chalk (36 parts), oil (2 parts), blue to shade, boiled as stiff as possible

Note.—The chasing closes up the threads and gives the starched back a thready appearance The subsequent facing up further stiffens the cloth and fills the face.

Example of Treatment for Twills.

(*a*) Fine twills for home trade.

Runs.—Water mangle, dry and condition for beetling, stiffen in two-wood mangle with light pressure, dry, damp, and stretch to pull up the twill

(*b*) Common waste twills for linings.

Runs.—Water mangle, dry and condition, three nips at calender, stiffen at B F M (back filling mangle), dry, condition, stretch, and add another light back at B F M, dry, condition, calender (swiss), starch at two-wood (heavily), dry, damp, stretch. The last drying will raise the figure of the twill

Example of Treatment for Drills.

(*a*) **Runs.**—Water mangle, dry and condition, stiffen on two-wood mangle, dry up, damp, and stretch

(Care must be taken to keep the selvages well turned out, and sharp scrimp rails must be used for this purpose.)

(*b*) Water mangle, dry and condition, beetle pure for brightness, stiffen on B.F.M, dry and condition, wind on (finishing frame) for room. The stiffening of the back in the B F M. and subsequent drying serve to throw up the face of the drill

Sheetings are treated in various ways, according to their quality and finish required, as shown by the following four examples of typical runs:—

Stretch, dry and condition in open, fold in halves if necessary to suit the widths of the succeeding machines, then proceed in either of the following ways:—

1.	2.	3.	4.
Stretch Condition	Stretch Stiffen Dry and condition	Stretch Beetle	Stretch Beetle Stiffen Dry and condition Stretch

Example of a "Betty Dodd" or Back-starching Mangle Finish.—This is given to illustrate one of the uses of the above method of stiffening, and to indicate how it may serve, in conjunction with other processes, to improve the utility and completely alter the apparent quality of a cloth. The grey cloth treated was of low count (14×10), and the finished appearance is that of a closely woven material, with a bright pure face, a smooth starchy back, and no sign of any space whatever between adjacent threads. It is thin, and the threads flat, but pliable, and suitable for any purpose that would be fulfilled by a thin calico, until washed. The particular use in this case is for sample seed-bags.

Making.—15 quarts each of maize and potato starch, 15 gallons china clay, 6 lbs. soap, blue to shade, and the whole diluted with water to 50 gallons and heated to 160° F.

Runnings.—Dry up at tins, damp, and three nips at calender, to close, flatten and smooth the threads, stiffen with above making in back starcher, drying immediately, on the large cylinder connected therewith, damp, beetle (30′ and 40′) to room

Alternatively to beetling as above, the cloth may be stretched and chased three times round, at calender, but the closing and smoothness will not be quite so complete.

Similarly, a better effect as regards initial closing is obtained by beetling than by the three heavy nips through the calender, but the value of the finished cloth does not warrant the expense

It may be remarked, in conclusion, that the art of finishing cannot be carried out with success by mere reference to a text-book, or by following formulæ alone, yet the consideration and analysis of published formulæ, of which there are many, affords a means for the exercise and development of inductive reasoning, which is perhaps the most important faculty required in the solution of the varied problems which arise in finishing

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